THE CRYSTAL AND MOLECULAR STRUCTURE OF 18-CROWN-6•$HgCl_2$ AND 18-CROWN-6•$CdCl_2$

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Abstract

$Hg(18\text{-Crown-6})Cl_2$ and $Cd(18\text{-Crown-6})Cl_2$ are isostructural, space group $C\bar{1}$, $Z = 2$. For the mercury compound, $a = 10.444(2)$ Å, $b = 11.468(1)$ Å, $c = 7.754(1)$ Å, $\alpha = 90.06(1)°$, $\beta = 82.20(1)°$, $\gamma = 90.07(1)°$, $D_{obs} = 1.87$, $D_{calc} = 1.93$, $V = 920.05$ Å^3, $R = 4.66\%$. For the cadmium compound, $a = 10.374(1)$ Å, $b = 11.419(2)$ Å, $c = 7.729(1)$ Å, $\alpha = 89.95(1)°$, $\beta = 81.86(2)°$, $\gamma = 89.99(1)°$, $D_{obs} = 1.61$, $D_{calc} = 1.64$, $V = 906.46$ Å^3, $R = 3.95\%$. The mercury and cadmium ions exhibit hexagonal bipyramidal coordination, with the metal ion located on a centre of symmetry in the plane of the oxygen atoms. The main differences between the two structures are an increase in the metal-oxygen distance and a reduction in the metal-chloride distance when the central ion changes from Cd^{2+} to Hg^{2+}. These differences may be explained in terms of the differences in hardness or softness of the metal ions and the donor atoms.

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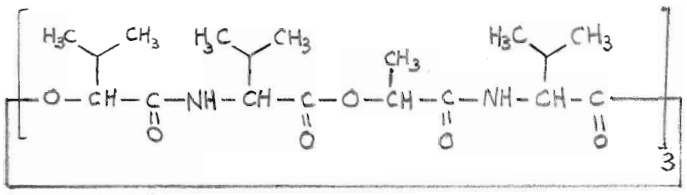
Section 1 Introduction

Interest in synthetic, multidentate, macrocyclic compounds has grown rapidly since the first reported synthesis (1) of the "crown-ethers" in 1967. This interest manifests itself in a variety of areas, ranging from attempts to synthesize new macrocyclic molecules of ever-increasing complexity and specificity of purpose, to attempts to find significant practical applications in such fields as isotope separation (2) and catalysis (3).

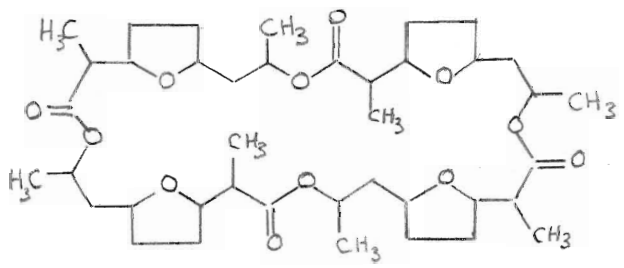
The field of macrocyclic synthesis has received thorough review (4), while the commercial potential of macrocyclic compounds for such diverse applications as isotope separation (2), catalysis (3), liquid membrane separations (5) and development of ion-selective electrodes (6) has received some attention (7).

Macrocyclic compounds find many uses other than those mentioned so far. They are able in some instances to render salts (e.g., $KMnO_4$ or KOH) soluble in benzene and other aromatic hydrocarbons, thus increasing their usefulness for organic oxidation or base reactions. Ionic species such as Sn_9^{4-} or Pb_5^{2-} can be isolated as salts of crown-solvated alkali ions (8). Cram and Cram have suggested (9) the resolution of racemic amino-acids with an optically active cyclic ether, by either liquid-liquid extraction or chromatography.

The crown-ethers in particular have interesting similarities to other, naturally-occurring, macrocyclic compounds. For instance, valinomycin and nonactin are ether-donors (see Fig. 1), which are involved in the formation



Valinomycin



Nonactin

Figure 1. Naturally-occurring, macrocyclic ether donors

of specific complexes with metal cations and certain hydrophilic, organic cations. Such macrocyclic organic molecules, called ionophores, provide a means of discriminating between pairs of cations (Na^+/K^+ and Mg^{2+}/Ca^{2+}) of a similar nature, by the cell membrane during transport in living systems. The important features studied, using crown-ethers as models of ionophores, include the following:

(a) The cell membrane is in essence an apolar, lipid bilayer, containing polar sites.

(b) In most natural systems the cell membrane preferentially takes up a cation from an aqueous, surrounding medium and, during transport, the ionophores involved separate the cation from its accompanying anion and solvating liquid (10, 11).

The complexes formed by the crown-ethers offer the possibility of a wide range of, often novel, coordination geometries for many cations. The present work was designed to investigate this aspect of one of the crown-ethers, namely 18-crown-6, with the cations Hg^{2+} and Cd^{2+}.

1.1 Structures of Polyoxa Crown Ethers and their Complexes

The field of macrocyclic chemistry embraces such a wide range of potential ligands (including thio-ethers, mixed oxa-thio ethers, aza-crowns and others) that in a work of this nature it is necessary to be specific. Attention will therefore be restricted to only the oxygen-donor macrocyclic compounds, or "crown-ethers".

They are macrocyclic polyethers in which donor oxygen atoms are arranged in a ring, being separated from each other by (usually) two methylene groups. The rings involved vary in size, containing anywhere from 4 to 20 oxygen atoms. The ring may carry aromatic nuclei (see Fig. 2). The "crown" nomenclature was established in the interests of brevity; compare 1,4,7,10,13,16-hexaoxacyclooctadecane to 18-Crown-6. The first numerals in the crown description describe the total number of atoms in the macrocycle, while the final numeral describes the number of donor atoms.

A detailed description of the crown ethers will be found in (1, 15 and 16). An up-to-date review of the structural and coordination chemistry of macrocyclic compounds in general, including their complexes will be found in references 12-14.

The complexes have a 1:1 or 1:2 (sandwich) or 2:1 (bimetallic) stoichiometry with respect to salt:crown. Bimetallic complexes are those in which two cations are complexed in the crown cavity. The first report (1) suggested that the complexation of a crown-ether with a cation had a stoichiometry determined basically by the fit of the cation in the ligand cavity. For crown-cation combinations having the best fit, 1:1 complexes were believed to be formed, both in solution and in the solid state. In

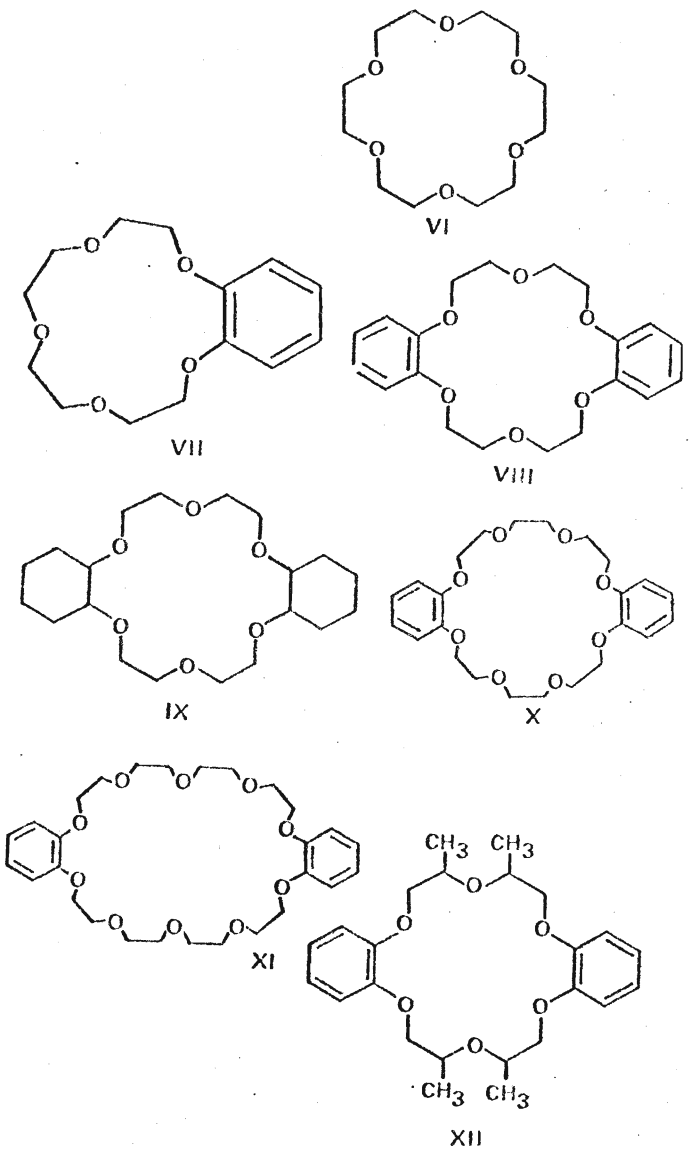


Figure 2. Some representative crown-ethers.

such complexes the donor oxygen atoms of the ligand were arranged about the cation in equatorial positions, with the axial sides of the cation exposed to the anionic species (Fig. 3 i; Fig. 4, top).

For increasing cavity size of the crown ether, 1:1 complexes still form, but there is a tendency for the ligand to be folded about the cation (Fig. 3 ii, iii; Fig. 5, bottom). Alternatively, bimetallic complexes are formed in which two cations are complexed in the cavity of the unfolded ligand (Fig. 3 iv; Fig. 5, top).

In situations where the size of the cation exceeds the cavity size of the crown-ether, 1:2 or 2:3 complexes are formed. The 1:2 complexes are described as "sandwiches" (Fig. 3, v; Fig. 5, centre) and the 2:3 complexes have been described as "club sandwiches" (Fig. 3, vi). These latter complexes have proven on detailed examination (17) to have actual stoichiometries of 1:1, with an extra molecule of the crown ether loose in the lattice.

Figure 3, vii and Figure 4, bottom, show a class of 1:1 metal-crown complexes found to be dimeric in the crystal lattice. This stoichiometry seems to be an alternative, in the solid state, to the sandwich structure.

Until recently metal-macrocycle systems have been discussed mainly from the viewpoint of a consideration of the relative size of the metal ion and the ligand cavity (the "ion-cavity radius" concept).

It has been demonstrated however (16), that such systems are more completely explained by a consideration of the charge-density of the metal ion, the nucleophilicity of the anion and the conformation and flexibility of the macrocycle. It would appear that during complexation with low

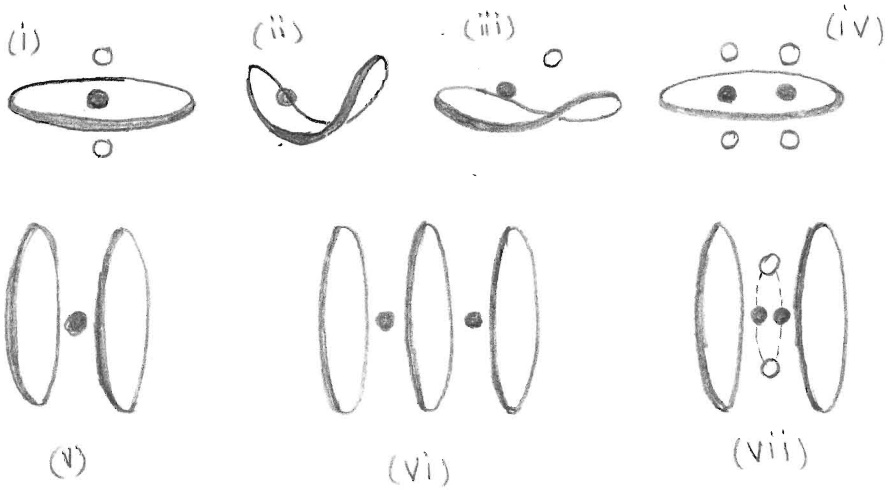
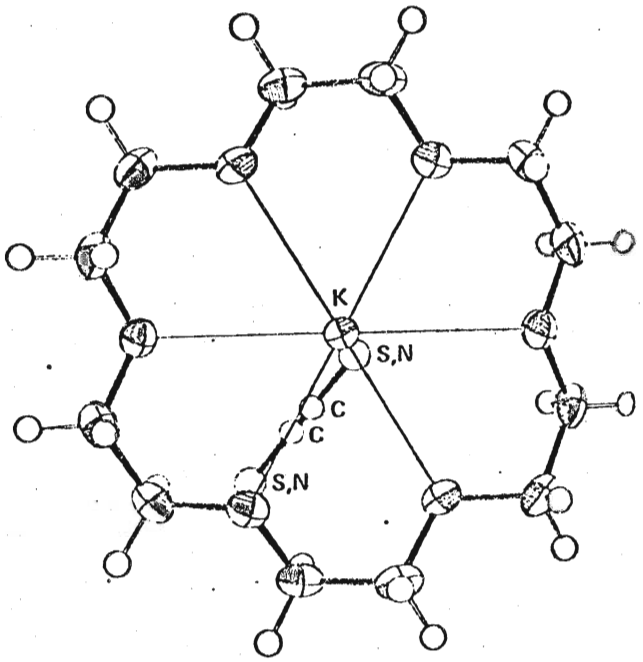


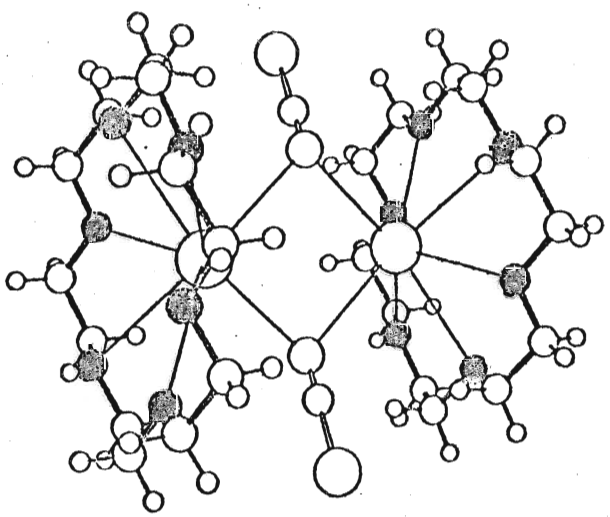
Figure 3. Configurations of crown complexes.
(Taken from Poonia, J. S., in ref. 16.)

Figure 4.



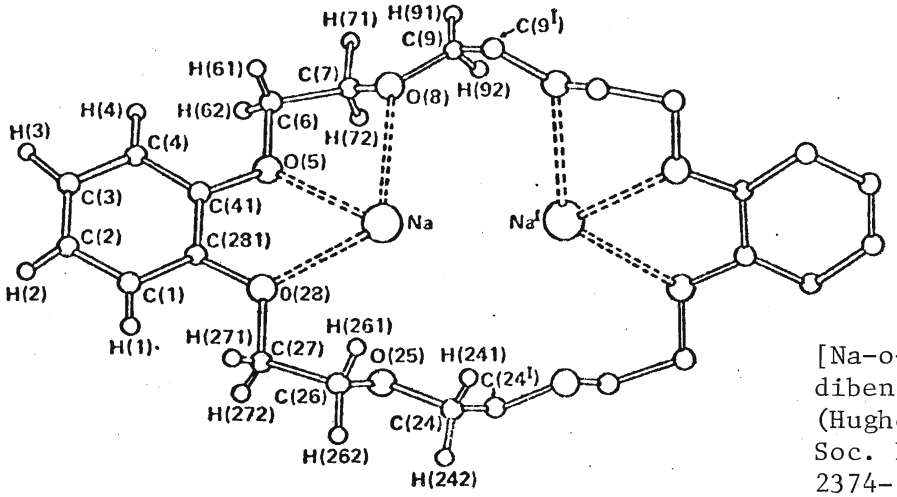
Structure of
KSCN·18-Crown-6

(Seiler, P., Dobler, M. and Dunitz, J. D. Acta Cryst. B30, 2744-2745 (1974)).



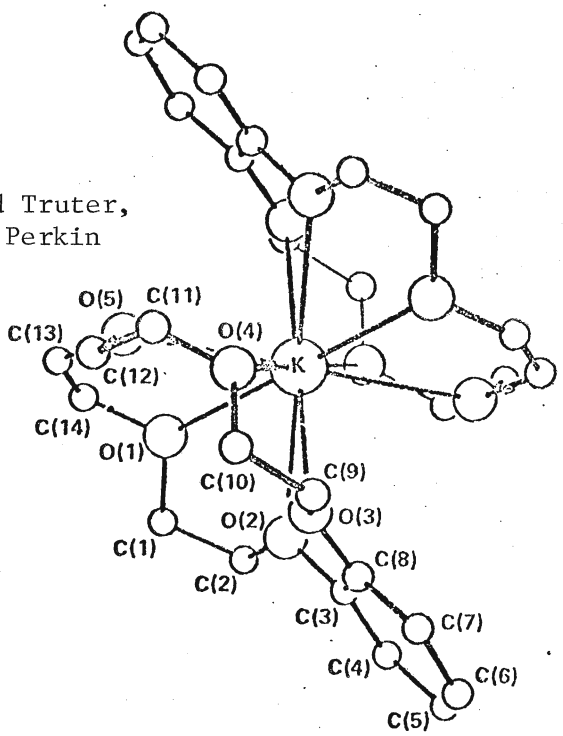
Structure of
CsSCN·18-Crown-6

(Dunitz, J. D., Dobler, M., Seiler, P. and Phizackerley, R. P., Acta Cryst. B30, 2733-2738 (1974)).

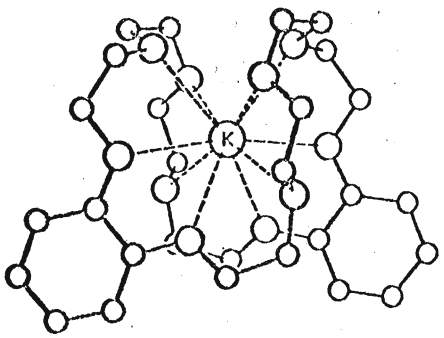


[Na-o-nitrophenolate-dibenzo-24-Crown-8] (Hughes, D. L., J. Chem. Soc. Dalton Trans. 2374-2378 (1975)).

Figure 5.

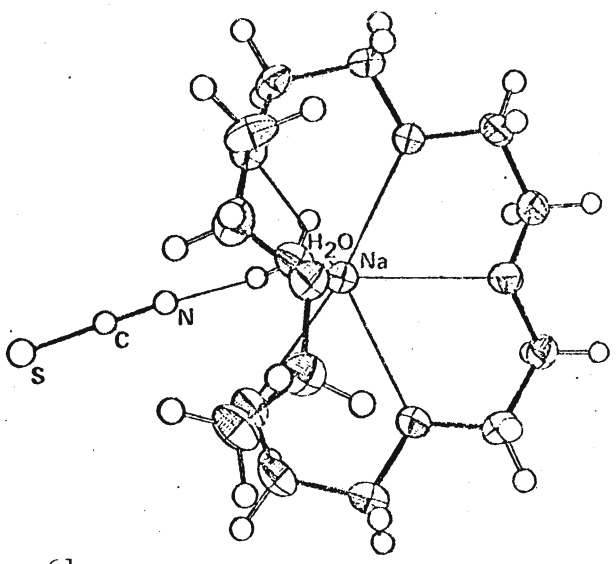


$[K\text{-}15\text{-}Crown\text{-}5]^+$ (Mallinson, P. R. and Truter, M. R., J. Chem. Soc. Perkin Trans. II, 1818-1823 (1972)).

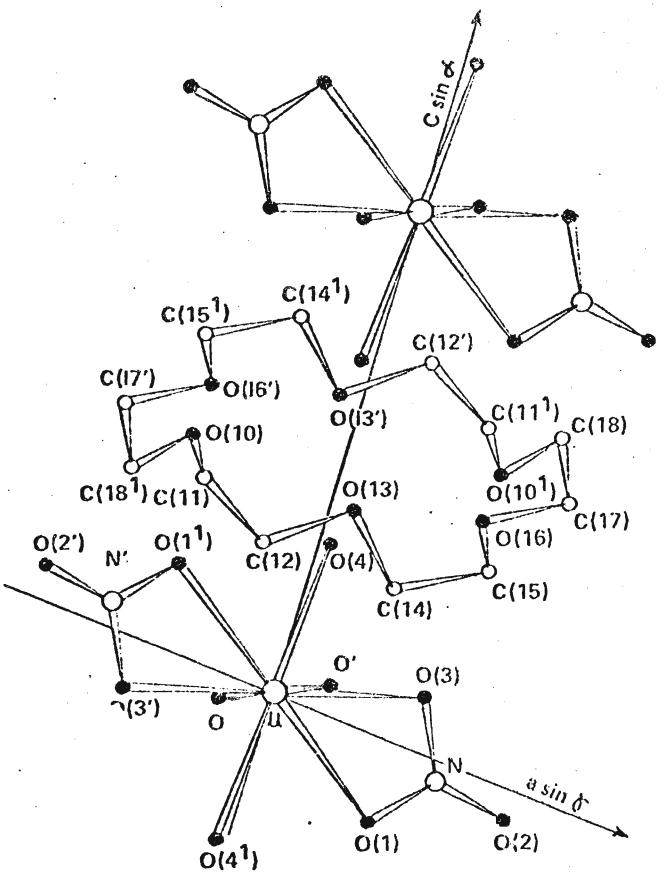


$[K\text{-}30\text{-}Crown\text{-}10]^+$ (Bush, M. A. and Truter, M. R., J. Chem. Soc. Perkin Trans. II, 345-350 (1972)).

Figure 6.



[$NaSCNH_2O$-18-Crown-6]
(Dobler, M., Dunitz, J. D. and Seiler, P., Acta Cryst. B30, 2741-2743 (1974)).

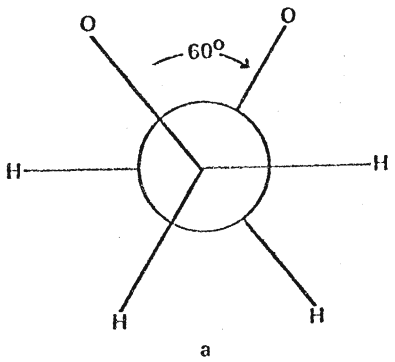


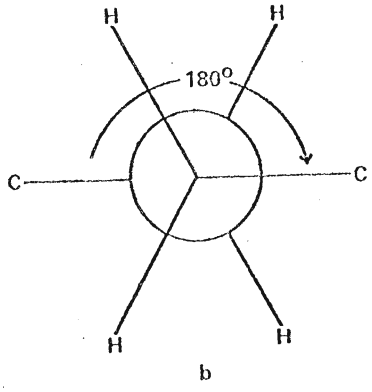
[$UO_2(NO_3)(H_2O)_2$]
(Bombieri, G., DePaoli, G., Cassol, A. and Immirzi, A., Inorg. Chimica Acta 18, L23-L24 (1976)).

charge-density cations (e.g., K^+) the crown-ether plays the dominant role, whereas in situations where high charge-density cations are involved (e.g., Mg^{2+}), the cation itself is the most important factor in the complexation.

For those complexes in which the cation is accommodated in the cavity of the crown and for those in which the cation lies above the cavity, the conformations of the ligands are similar. The torsion angles exhibit values indicative of a low level of torsional strain. The O-C-C-O torsion angles are near 60° and the C-C-O-C angles are near 180° (Fig. 7). In those cases where the cation is smaller than the ligand cavity, and ligand wrapping of the cation (or complexation with two cations) occurs, or in those structures where the cation does not complex with all the potential donor atoms, deviation of the torsion angles from the previously stated values occurs.

The following tabulated data are taken from the most recent original papers, and exclude structural information relating to mixed donor or other macrocyclic compounds. This exclusion is consistent with the defined purpose of this section of the thesis. For a more comprehensive account of macrocyclic complexes, the reader should consult reference 14.





(a) O–C–C–O torsion angle of 60°.
(b) C–C–O–C torsion angle of 180°.

CLOCKWISE = +

Figure 7. Torsion angles and their sign convention.

Table 1. Recent Structures of 18-Crown-6 Complexes

Cation	Anion	Ligand-Metal Ratio	Reference	Description of Coordination Geometry
La^{3+}	NO_3^-	1:1	23	La is 12-coordinated to 6 polyether O atoms, to 2 bidentate NO_3^- ions on one side of the crown and a third NO_3^- on the other side.
Nd^{3+}	NO_3^-	1:1	24	Nd is 10-coordinated to 3 bidentate NO_3^- groups and the 6 polyether O atoms. The macrocyclic conformation is "boat".
Gd^{3+}	NO_3^-	1:1	23	The crown-ether is not coordinated to the Gd. $[Gd(NO_3)_3(OH_2)_3]$ contains the 9-coordinated Gd^{3+} The crown-ether is bound to the coordinated water molecules.
Complex with dimethyl sulphone		2:1	25	One methyl group of each dimethyl sulphone has three C-H...O contacts to alternate polyether O atoms.
Complex with guanidinium nitrate		2:1	26	Unit cell contains 2 centrosymmetric units [nitrate-guanidinium-18-Crown-6-guanidinium-nitrate] linked via a guanidinium hydrogen atom to one polyether O, and from a second guanidinium hydrogen atom to one oxygen atom of the nitrate ion.
$[Mn(H_2O)_6]^{2+}$	ClO_4^-	2:1	27	No direct Mn-O polyether bonds formed. $Mn(H_2O)_6$ group is hydrogen bonded to the polyether O atoms.
$MnNO_3(H_2O)_5^+$	NO_3^-	1:1	28	The 5 O atoms from water molecules and one O atom from the nitrate group form the vertices of a distorted octahedron around the Mn, giving a univalent complex cation. This complex cation is connected to the polyether molecule by 2 coordinated water molecules via hydrogen bonding.

Table 1, p. 2. Recent structures of 18-Crown-6 Complexes

Cation	Anion	Ligand-Metal Ratio	Reference	Description of Coordination Geometry
$[Co(H_2O)_6]^{2+}$	$[CoCl_4]^{2-}$	1:1	27	No direct Co-O polyether bonds formed. Hydrogen bonds between polyether O and $Co(H_2O)_6$ group.
NH_4^+	Br^-	1:1	29	The ammonium cation is displaced by 1.00 Å from the mean oxygen plane of the 18-Crown-6 and also interacts with the nearest bromide ion.
Benzyl ammonium	NCS^-	1:1	30	The benzylammonium cation forms three hydrogen bonds to 3 alternate oxygen atoms of the polyether.
$[trans\text{-}PtCl_2(PMe_3)NH_3]$		1:2	31	The ligand binds two molecules of the platinum ammine, one to each face of the crown. All 6 of the polyether oxygens are hydrogen bonded in an approximately trigonal fashion to the two NH_3 groups.
$[Cu(NH_3)_4H_2O]^{2+}$	$[PF_6]^-$	1:1	31	A chain copolymer is formed in which each individual crown molecule is involved in 10 hydrogen bonds with 4 ammine ligands coordinated to the Cu(II) centres in adjacent ions.
$[bis\text{-}(ED)Pt]^{2+}$	$[PF_6]^-$	1:1	31	A chain copolymer in which the metal complex is sandwiched between two crown molecules that are laterally displaced so that each ethylene diamine ligand is involved in two hydrogen bonds to oxygen atoms, and each 18-Crown-6 ring in four hydrogen bonds.

It has been stated (18) that shorter than usual C-C bonds are observed in all cyclic polyethers and their complexes studied to date, but that no satisfactory explanation of this has been given.

In closing this section, the following points should be borne in mind while examining the structures of the complexes of $HgCl_2$·18-Crown-6 and $CdCl_2$·18-Crown-6 which form the basis of this work:

(i) Which type(s) of structure summarized in this section is/are adopted by the new complexes?

(ii) Are the torsion angles within the ranges exhibited in known complexes of a similar type?

(iii) What is the coordination number and geometry of the metal ion in each of the compounds?

Consideration of the bond lengths and coordination geometry typical of Hg(II) and Cd(II) is the next subject for review, and forms the basis for Section 1.2.

1.2 The Stereochemistry of Cd(II) and Hg(II) Compounds

This review will be restricted to the consideration of molecules and ions that are predominantly covalent in character, and will omit the cases where coordination takes place in a simple ionic crystal.

It is common today to call any atom or polyatomic species bonded to a central atom a "ligand". For example the fluorine atoms in the molecule SF_6 are termed ligands just as the ammonia molecules are in the ion $[Co(NH_3)_6]^{3+}$. This practice will be followed throughout the discussion.

The structures of the compounds to be discussed will be reviewed using two properties, namely, coordination number and coordination geometry. By coordination number is meant the number of outer, or ligand, atoms bonded to the central one. Coordination geometry is to be understood to mean the geometric arrangement of these ligand atoms and the consequent symmetry of the compound (31). Coordination geometry is most usually described in terms of the polyhedron described by the joining together of the ligands by straight lines (e.g., the 4 hydrogen atoms surrounding a carbon atom in CH_4 produce a tetrahedron when joined by straight lines).

The shapes of these regular polyhedra associated with a given coordination number have been exhaustively reviewed in reference (32).

The maximum stable coordination number of an atom is influenced by the following factors:

(a) The size of the central atom and the ligand.

(b) Oxidation state of the central atom.

(c) The principle of electroneutrality.

(d) Electronegativity of the ligand.

(e) The orbital energies.

(f) The bond type.

(g) The "nine orbital rule".

A detailed discussion of each of these factors will be found in reference 33. For the purpose of this review, it is proposed to summarize the range of coordination number exhibited by Cd and Hg in only one oxidation state, namely +2. Specific examples of typical compounds exhibiting these particular coordination numbers have been obtained from the literature, along with stereochemically important data, such as bond angles, bond lengths and the shape of the coordination polyhedron. The types of coordination manifested by Cd(II) and Hg(II) will finally be compared together. The data have been tabulated for convenience. Where a particular coordination geometry has not been reported for either Cd(II) or Hg(II), a blank space has been left in the table. All bond lengths and angles are about the metal atom, unless stated otherwise.

Table 2. Coordination numbers 2-7.

Reference	Compound	Bond Length (Å.U.)	Bond Angles (°)
Two Coordination; linear molecules			
34	$Hg(Me)_2$	Hg-C 2.094	180°
	$Cd(Me)_2$	Cd-C 2.112	180°
Two coordination; angular			
35	$Hg(CN)_2$	Hg-C 2.1	171°
Three coordination; trigonal planar			
36	$Me_4N^+HgBr_3^-$	Hg-Br 2.52	121.8, 114.4, 119.1
	$Me_3S^+HgI_3$	Hg-I 2.72, 2.69, 2.72	124, 113, 123
Four coordination; square planar			
38	$HgCl_2$·1,4-dioxane	Hg-O 2.66 Hg-Cl 2.34	not available
Four coordination; tetrahedral			
39	Hg(tetb)Cl_2	2.420-2.528	Cl-Hg-Cl 95.0
40	$HgCl_2(Ph_3AsO)_2$	HgCl 2.32, 2.33 Hg-O 2.32	Cl-Hg-Cl 146.5 O-Hg-O 92.5
41	$Cd(NH_3)_4^{2+}$	2.10	not available
42	$CdCl_2$(thiourea)$_2$	Cd-Cl 2.51 Cd-S 2.45	Cl-Cd-Cl 103° Cl-Cd-S 106° S-Cd-S 129
Five-coordination; trigonal bipyramid			
43	$CdZn(PO_4)_2$	Cd-O 2.16-2.31	166 (distorted)

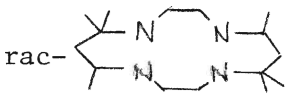
tetb ≡ rac- 

Table 2 (cont'd.)

Reference	Compound	Bond Length (Å.U.)	Bond Angles (°)
Five-coordination; square pyramid			
44	$[Hg(La)Cl]^+$	Hg-Cl 2.46 Hg-N 2.28-2.42	N-Hg-N 82.5-86.4
	(La ≡ 1,4,8,11-tetra-azacyclotetradecane)		
(44) Structural data from diffractometry is not available for the equivalent cadmium nitrate complex, but ^{113}C NMR studies indicate a mixture of isomers, which interconvert at elevated temperatures, one isomer having a structure equivalent to that of the Hg structure outlined above.			
Six coordination; octahedral			
45	$KHg(CN)_2I$	Hg-C 2.08 Hg-I 3.38	CN-Hg-CN linear
46	$HgCl_2 \cdot$(tetb)	Hg-Cl (bridging) 2.421 Hg-N 2.439, 2.275	Very distorted octahedron (almost a trigonal prism)
47	$CdCl_2(urea)_2$	Cd-Cl 2.52 Cd-O 2.28	Cl bridges, angles ~90°
Seven coordinate; pentagonal bipyramid			
48	$HgBr_2 \cdot L_b$	Hg-O 2.72-3.06 Hg-Br 2.387, 2.409	O-Hg-O 60.5-62.5
49	$[CdL^3(Br)]^+$	Cd-Br 2.582 Cd-N 2.335-2.452	N-Cd-N 67.4

L_b L_b ≡ 1,15-Bis(2-bromophenyl)-2,5,8,11,14-pentaoxapentadecane

L^3 ≡ 2,15-Dimethyl-3,7,10,14-20-penta-azabicyclo[14.3.1]-eicosa-1(20),2,14,16,18-pentaene

The complex $HgCl_2 \cdot tetb$ is, I believe, unique in that it contains both tetrahedrally and octahedrally coordinated Hg^{2+}.

The complex with ligand L_b is interesting as being almost a crown ether. It is similar to complexes of $HgCl_2$ reported in reference 50. The bond lengths are approximately the same as those found in the crown ligand diaza-18-Crown-6 complexing with HgI_2. Eight coordination for Hg(II) and Cd(II) is relatively rare. The summary, in Table 3, is complete to date.

Eight-coordination may occur in a number of idealised geometries, namely; cubic, square antiprismatic, dodecahedral, hendecahedral, symmetrically bicapped trigonal antiprismatic (or puckered hexagonal bipyramidal) and hexagonal bipyramidal(32).

The factors which may be expected to influence the choice of configuration are (33):

(i) Direct bonding interactions

(ii) Mutual repulsion of the ligands

(iii) The presence of non-bonding lone pairs

(iv) The geometrical restrictions of the ligand stereochemistry.

The most common arrangements of eight ligands about a central atom are the square antiprismatic and the dodecahedral, both of which may be regarded as distortions of a cubic arrangement of ligands. There appears to be little difference between them energetically.

The occurrence of hexagonal bipyramidal coordination is virtually unknown in the cases of Cd(II) and Hg(II); in fact, to date, only (55) is a known example. This type of coordination has previously been confined

largely to the actinide series. When the distances between adjacent pairs of the six equivalent ligands are equal, then the hexagon is said to be puckered. If these distances are alternately long and short, then the hexagon is planar.

A reasonable explanation for the adoption of this rare configuration is advanced in the section of the thesis dealing with the coordination of the metal ions.

Table 3. Eight coordination; square antiprism or dodecahedron

Reference	Compound	Bond Length (Å)	Bond Angles (°)
51	$K_3[Hg(NO_2)_4]NO_3$	Hg-O 2.39-2.57	distorted square antiprism
52	$Hg(BrO_3)_2 \cdot 2H_2O$	$Hg-O_W$ 2.33, 2.34 $Hg-O_{BrO}$ 2.42, 2.72	O-Br-O 103.1 (neutron diff. in progress)
52	$K_2Hg(BrO_3)_2(NO_3)_2$	$Hg-O_{NO}$ (4 x 2.589) $Hg-O_{BrO}$ (4 x 2.434)	O-Hg-O 180; O-Br-O 102.9 O-Hg-O 72
53	$Cd(NO_3)_2 \cdot 4H_2O$	$CdO_{H\ O}$ 2.26, 2.33 CdO_{NO} 2.44, 2.59	Distorted dodecahedron
54	$Cd(BrO_3)_2 \cdot 2H_2O$	Cd-O 2.73; 2.33-2.53	Preliminary report
52	$K_2Cd(BrO_3)_2(NO_3)_2$	Study still in progress (Dec. 1981); it is believed the structure is identical with (52) above.	

Eight coordination; hexagonal bipyramid

55	HgI_2·Diaza-18-Crown-6	Hg-O 2.909-2.935 Hg-I 2.680 O-Oi 5.582 N-Ni 5.448 Hg-N 2.724	IHgO 83.7-93.9
55	CdI_2·Diaza-18-Crown-6	Cd-O 2.811-2.841 Cd-I 2.827 O-Oi 5.652 N-Ni 4.964 Cd-N 2.482	ICdO 85.9-94.1

Table 4. A Comparison of the Stereochemistry of CdII and HgII.

Shape of molecule	Coordination Number	Observed for Hg	Observed for Cd	Example(s) of a structure exhibiting this coordination	
linear	2	yes	yes	$Hg(Me)_2$	$Cd(Me)_2$
angular	2	yes		$Hg(CN)_2$	
trigonal planar	3	yes		$(CH_3)_3S^+$ HgI_3^- Me_4N^+ $HgBr_3^-$	
pyramidal	3				
tetrahedral	4	yes	yes	$HgCl_2$(tetraazamac) $Hg(SCN)_4^{2-}$	$Cd(NH_3)_4^{2+}$ $CdCl_2(thiourea)_2$
square planar	4	yes		$HgCl_2 \cdot 1,4$-dioxane	
trigonal bipyramid	5		yes		$Cd_2Zn(PO_4)_2$
square pyramid	5	yes	yes	$[Hg(La)Cl]^+$ (a)	$[Cd(La)]^{2+}$ $[NO_3]^{2-}$ (a)
octahedral	6	yes	yes	$KHg(CN)_2I$ $HgCl_2 \cdot$(tetraazamac)	$CdCl_2(urea)_2$
pentagonal bipyramid	7	yes	yes	$HgBr_2 \cdot Lb$ (b)	$[CdL^3(Br)]^+$
square antiprism or dodecahedron	8	yes	yes	$K[Hg(NO_2)_4]NO_3$ $Hg(BrO_3)_2 \cdot 2H_2O$ $K_2Hg(BrO_3)_2(NO_3)_2$	$Cd(NO_3)_2 \cdot 4H_2O$ $Cd(BrO_3)_2 \cdot 2H_2O$ $K_2Cd(BrO_3)_2(NO_3)_2$
hexagonal bipyramid	8	yes	yes	$HgCl_2 \cdot$18-Crown-6 $HgI_2 \cdot$diaza-18-Crown-6	$CdCl_2 \cdot$18-Crown-6 $CdI_2 \cdot$diaza-18-Crown-6

Table 4, p. 2.

Notes:

(a) La is equivalent to 1,4,8,11-tetra-azacyclotetradecane

(b) Lb is equivalent to 1,15-bis(2-bromophenyl)-2,5,8,11,14-pentaoxapentadecane

Section 2 Experimental

2.1 Crystal growth, selection and density determination

The method employed for crystal growth differs slightly for each of the two complexes prepared.

(a) Preparation of the $HgCl_2$·18-Crown-6 complex

The complex between $HgCl_2$ and 18-Crown-6 was prepared by dissolving 0.26 g of the 18-Crown-6 in 20 mL of hot 1-butanol and allowing this solution to cool standing in ice. An equimolar quantity (0.27 g) of $HgCl_2$ (reagent grade) was dissolved in hot 1-butanol and also allowed to cool, standing in ice. In neither case did any solid come down out of solution. Both clear solutions were then reheated almost to boiling, then mixed in a 100 mL flask. The flask and contents were clamped in a 600 mL beaker filled with very hot water. This apparatus was left for 18 hours, when well-shaped, translucent crystals were found deposited on the bottom of the flask. These were filtered off at the pump, washed with several small portions of ice-cold 1-butanol, then allowed to dry in a vacuum desiccator.

(b) Preparation of the $CdCl_2$·18-Crown-6 complex

The preparation was essentially the same, but in this case the solvent for the $CdCl_2$ was distilled water. The $CdCl_2$ was reagent grade, 0.23 g being taken as a quantity equimolar to 0.26 g of 18-Crown-6.

The same procedure of dissolving the solids in hot solvent and cooling was followed. However when the two hot solutions were mixed and allowed to stand in the beaker of hot water, the 1-butanol solution formed a separate layer floating on the water. After 3 hours small crystals formed at the interface and these grew for a further 15 hours until they were filtered off and treated as before.

The crystals were shiny, well-formed and transparent.

Crystals potentially suitable for study by X-ray diffraction were selected by examination with a polarising microscope. The criteria used for selection were size, regularity of shape, the absence of visible cracks or surface irregularities and the sharpness of the extinctions when the crystal was rotated in plane polarized light.

In both cases suitable crystals were mounted on thin glass fibres using Lepage's Five Minute Epoxy and submitted to a preliminary examination by X-ray photography. The appearance of the oscillation and zero level Weissenberg photographs was used in selecting a crystal of each complex for subsequent data collection on an automated diffractometer.

Following the selection of suitable crystals, the density of each compound was determined by flotation using a mixture of carbon tetrachloride and dibromoethane. The results of the density determination together with the calculated density are presented in Table 10, along with the details of the intensity collection, crystal size and least squares refinement.

Samples of each complex were sent for microanalysis. Carbon and hydrogen analyses were performed by Guelph Chemical Laboratories, Ltd., while heavy metal analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee. Calculated for $HgCl_2$·18-Crown-6: 26.89 % C, 4.48 % H, 37.46 % Hg; Found: 27.19 % C, 4.87 % H, 37.68 % Hg. Calculated for $CdCl_2$·18-Crown-6: 32.19 % C, 5.37 % H, 25.13 % Cd; Found: 32.16 % C, 5.53 %H, 24.98 % Cd.

2.2 Weissenberg photography

For each complex, 15 ° oscillation photographs were taken with the crystal mounted along the longest axis. A Picker X-ray unit was used with a Weissenberg camera from the Charles Supper Company. Kodak No-Screen Medical X-ray film was used, with fifteen minute exposures to unfiltered CuKα radiation. The films were processed using Kodak D19 developer and X-ray Fixer. Crystal alignment was carried out using the methods described in Stout and Jensen (56).

Once the alignment was correct, the above apparatus was used to take equi-inclination Weissenberg photographs. Nickel-filtered CuKα radiation was used (λ = 1.5418 Å) with exposure times of approximately fifteen hours.

In both cases the hk0, hk1 and hk2 layers were photographed using layer line screen shifts and inclination angle settings based on the lattice dimensions obtained from the oscillation photographs. The methods used to obtain these dimensions, shifts and settings are described in Stout and Jensen (56).

As the analysis of the photographs is, for all intents, the same, a description of the reasoning will be given for only $HgCl_2$·18-Crown-6.

An initial inspection of the oscillation photograph indicated no left-right symmetry. Inspection of the zero layer Weissenberg seemed to show, on first examination, left-right symmetry about two potential axes separated by ninety degrees. However, a more careful scrutiny of the relative intensities of spots which should have been identical showed small differences.

It was concluded that the crystal was triclinic, exhibiting pseudo-monoclinic symmetry. The axes chosen as a* and b* were separated by approximately ninety degrees measured on the film. The indexing of the film on the basis of these axes showed systematic absences to be present with h + k odd, consistent with C-face centring. The space-group symbol was then the non-standard, triclinic $C\bar{1}$.

With the approximate cell dimensions and angles known, the crystal was now submitted to investigation on the diffractometer.

2.3 Diffractometry using the Enraf-Nonius CAD-4

For a single crystal of each complex, intensity data were measured with an Enraf-Nonius CAD-4 diffractometer controlled by a PDP-8a computer, using graphite-monochromatized MoKα radiation. The orientation matrix and accurate cell dimensions were obtained by least-squares refinement on the setting angles of twenty-five centred, strong reflections with $9° < \theta < 22°$. The intensity of a standard reflection was measured every hour as a check on instrument and crystal stability. No systematic variation was observed.

Crystal orientation was also checked every one hundred reflections by recentring 3 axial reflections. Crystal recentring was at no time necessary. The intensities were measured in both cases by the $\omega/2\theta$ scan technique. The scan speed was adjusted, after a prescan at two degrees per minute, to make $I/\sigma(I)$ equal 100; a maximum time scan of 300 seconds was imposed. The background was measured for one-quarter of the scan time at each of the scan limits.

Table 5. Details of the Intensity Collection and the Least Squares Refinement

	$HgCl_2$·18-Crown-6	$CdCl_2$·18-Crown-6
Formula Weight	535.5	447.3
D_{calc} (Mg m^{-3})	1.933	1.639
D_{exp} (Mg m^{-3})	1.87	1.61
Crystal size (mm)	0.05 x 0.16 x 0.70	0.04 x 0.28 x 0.8
Radiation	Graphite monochromatized MoKα	
Take-off angle (°)	4.35	4.35
θ interval (°)	1-25	1-25
Scan type/width	ω-2θ/ 0.7 + 0.35 tan θ	ω-2θ/ 0.7 + 0.35 tan θ
Maximum recording time (s)	300	300
μ (cm^{-1})	85.6	14.59
Range of transmission factor	0.23-0.65	--
Number of measured reflections	4280	3200
Number of reflections with zero weight ($I < 3\sigma(I)$]	0	7
Number of reflections used in the final refinements	1621	1600
Number of parameters refined	98	98
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0466	0.0395
$R_w = \|\sum w(\|F_o\| - \|F_c\|)^2/ \sum w\|F_o\|^2\|^{\frac{1}{2}}$	0.0418	0.0376

2.4 Data Reduction

Data reduction was carried out using the locally produced programme CONVI (see Appendix B). The programme was used to perform the following operations:

(i) Scale the data with reference to the attenuator, when this was used

The attenuation factor of the filter used was measured experimentally and found to be 13.1. Any reflection for which the data record indicated that the attenuation was set, was multiplied by 13.1 (see Appendix B, listing of programme CONVI, sequence 60-62).

(ii) Scale the data with reference to the standard reflection

The data between successive measurements of the standard were corrected according to the number of intervening reflections. All data were normalized to the initial intensity of the standard reflection (see Appendix B, listing of programme CONVI, sequence 47, 50-56).

(iii) Calculate the total background count and make allowance for this in the measured value of a reflection.

The net intensity of a reflection, I, was calculated from:

$$I = INT - 2*(BGL + BGR)$$

where INT is the peak count and BGL, BGR are respectively the background counts on the left and the right of the peak.

These background counts were measured for one-half of the scanning time (see Appendix B, listing of programme CONVI, sequence 26).

(iv) Calculate and correct for the Lorentz-polarization factors

A correction for the Lorentz effect was applied from:

$$L = 1/\sin(2\theta) \qquad (58)$$

where θ is the Bragg angle for the hkℓ reflection (see Appendix B, listing of CONVI, sequence 22).

A correction for polarization of the X-ray beam, by the graphite monochromator and the crystal plane, was calculated and applied from:

$$P = \frac{\cos^2(2\theta_m) + \cos^2(2\theta)}{1 + \cos^2(2\theta_m)}$$

where θ_m is the Bragg angle for the graphite monochromator (6.1 ° for MoKα radiation).

θ is the Bragg angle for the hkℓ reflection and the monochromator graphite crystal was assumed to be ideally imperfect in its mosaicity (57, see also Appendix b, listing of programme CONVI, sequence 20-25, 62).

(v) Scale the data with respect to the width of the scan and the speed of the scan

The variable omega width of the scan angle was corrected for by multiplying by the absolute value of the width, which was stored in the data record.

The variable scan speed was corrected for, by dividing by the absolute value of the scan speed, this data also being stored in the data record of the diffractometer (57).

(vi) The calculation of the standard deviation, σ(F) of the reflection, which will be used in the refinement to determine the weight of the reflection

Standard deviations were calculated using the equation

$$\sigma(F) = \frac{1}{2} \times \sqrt{\frac{INT + 4(BGL + BGR) \times WIDTH \times ATTEN}{LP \times FACTOR \times ABS(NPI) \times RAW}} \qquad (56,57)$$

where the qualities INT, BGL, BGR have the previously defined meaning.

ATTEN, the attenuation factor has the value 1.0 if the attenuator is not set, and the value 13.1 if it is set.

LP is the combined Lorentz-polarization factor previously discussed.

FACTOR is the correction factor for any diminution in the intensity of the standard reflection.

NPI is the variable scan speed factor, read from the original data record.

RAW = INT - 2*(BGL + BGR)

i.e., the observed intensity corrected for background.

At the time of writing, no correction had been applied for the effect of absorption, although it was realised that this would be important for the mercury complex due to its high absorption.

Section 3. Structure determination and refinement

The structures of $HgCl_2 \cdot 18\text{-Crown-6}$ and $CdCl_2 \cdot 18\text{-Crown-6}$ were determined by the heavy atom method. As the procedure followed was identical in both cases, it will be described in detail only for the Hg complex.

Both complexes are triclinic, space group $C\bar{1}$, the equivalent positions for which are shown in Figure 8.

As there are two molecules per unit cell, based on the density determination, the first mercury atom must occupy the position (0,0,0) so that the C-face centring operation may generate the second atom at $(\frac{1}{2},\frac{1}{2},0)$. Thus the asymmetric unit is one-half the molecule and consists of 3 oxygen atoms, 6 carbon atoms with their accompanying hydrogen atoms, one chlorine and one-half of a mercury atom.

With the first mercury atom fixed at (0,0,0), a difference Fourier map was plotted using the programme SHELX (58), the computations being performed on a Burroughs B6700 computer.

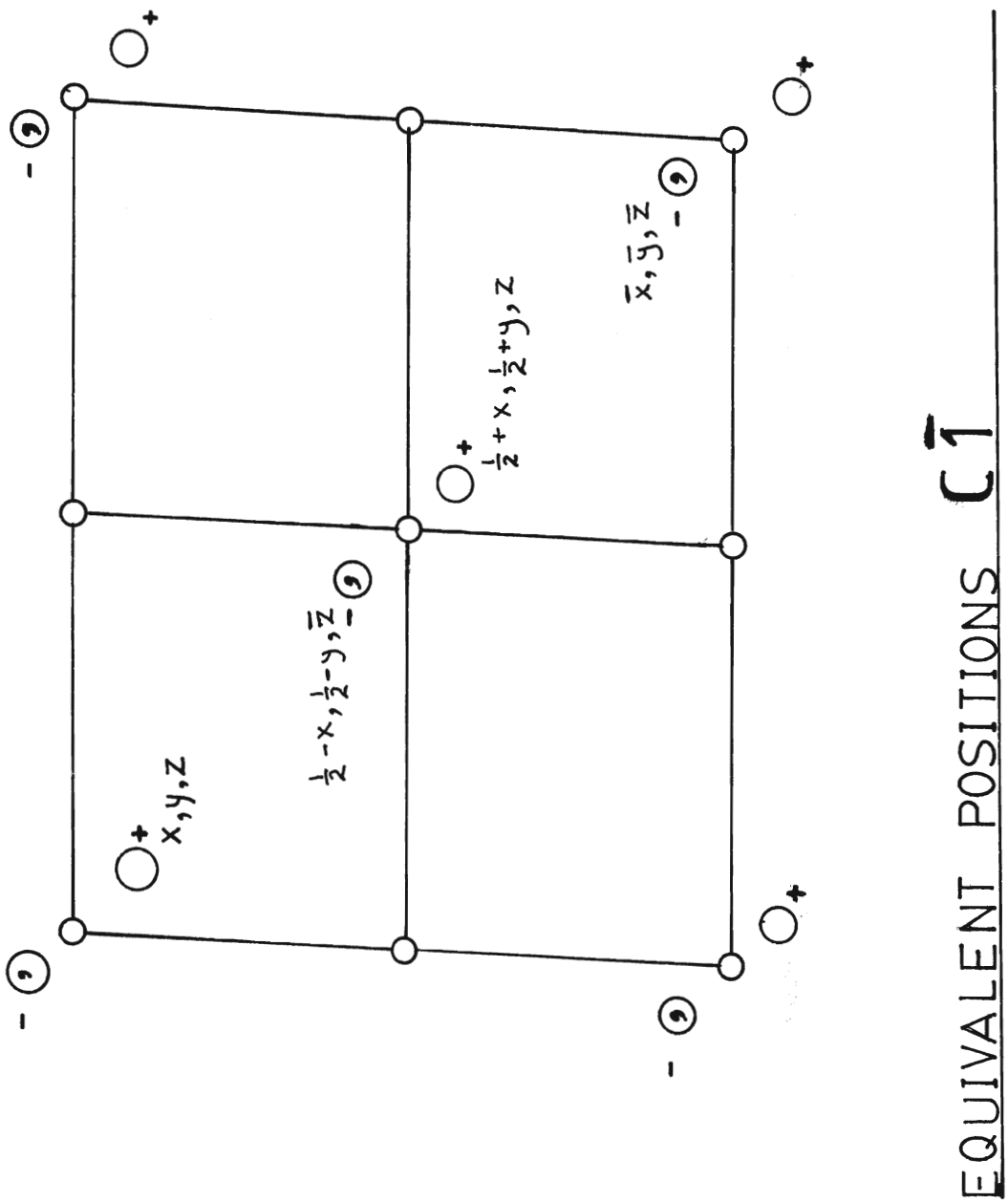
The Fourier expression that is used in calculating the difference in electron density between the postulated and observed structure may be expressed as

$$\Delta e(xyz) = \frac{1}{V} \sum_{hk\ell}\sum\sum\sum(|F_o| - |F_c|)\exp i\alpha \exp(-2\pi i(hx + ky + \ell z))$$

where α is the phase associated with F_c, the calculated structure factor.

If a structure has been satisfactorily solved and refined, then the calculation of a difference Fourier gives a measure of the correctness of

Figure 8. Equivalent positions $C\bar{1}$.



the crystal structure, since the calculated structure factor moduli are based on the crystal structure model. Any atoms which have not been found should show up on the difference Fourier.

The first difference Fourier yielded a peak (region of high electron density) at a distance of 2.33 Å from the mercury atom. This peak was assigned to a chlorine atom, the location of which was fixed and a second difference Fourier run.

As a result of this second difference Fourier, it proved possible to locate the entire asymmetric unit including hydrogen atoms. Up until this point, unit weights had been used with isotropic temperature factors. The agreement index R, defined as

$$R = \sum(|F_o| - |F_c|)/\sum|F_o|$$

had fallen from 43 % to 23 % with the locating of the Cl atom.

A third difference Fourier was now run with anisotropic temperature factors for all non-hydrogen atoms, the hydrogen atoms being allowed to ride on their attendant C atoms as a CH_2 group. A weighting scheme was introduced and three cycles of least-squares refinement were executed. The unweighted R-index then reached a figure of 4.4 % at which point, as no absorption correction could be applied, refinement was halted.

A refinement programme based on the least-squares procedure calculates structure factors and accumulates least-squares totals which are later solved for changes in various parameters. These parameters are treated as functions of $|F_c|$ and the least-squares procedure minimizes the function

$$\sum w(|F_o| - |F_c|)^2$$

where w is a weight allocated to each structure factor.

The parameters that were refined were:

(i) The $|F_o|$ scale factor.

(ii) The atomic coordinates.

(iii) The six components of the individual atomic anisotropic vibration tensors, U_{ij}.

Each observation has an associated weight which is used in the function minimized by the least-squares procedure $\sum w\Delta^2$. This weight should reflect the reliability of the particular measurement, and $w = 1/\sigma^2$, where σ^2 is the variance of the measurement due to random experimental errors and σ is the standard deviation.

In the programme SHELX (60) which was used for the refinement of both structures, the scattering factors were calculated from the analytical expression:

$$f(\lambda^{-1}\sin\theta) = \sum_{i=1}^{4} a_i \exp(-b_i\lambda^{-2}\sin^2\theta) + c$$

The coefficients a_i, b_i and c for Hg (and Cd) as well as the real and imaginary parts of the corrections for anomalous dispersion were taken from International Tables for X-Ray Crystallography (59) and from (60).

At the point where refinement was halted, the average parameter shift was less than 0.30 estimated standard deviations. During the last cycle a total of 98 variables were refined. For the 1621 independent reflections with $F \geqslant 3\sigma(F)$, the final R values were $R = 0.0466$ and $R_w = 0.0418$. The final difference map calculated showed a peak of magnitude equivalent to

3 electrons/Å^3 at a distance of 0.8 Å from the Hg atom, attributed to the presence of the heavy atom and to series termination errors. It was expected that when an absorption correction was applied, this peak should be much reduced. Other than that, no peaks or holes with magnitude greater than 0.8 electrons/Å^3 were observed (this peak being at 0.8 Å from the Cl atom) with the average figure being 0.3 electron/Å^3. The values for the equivalent cadmium information are: $R = 0.0395$ and $R_w = 0.0387$ with a maximum on the final difference map equivalent to 0.4 electrons/Å^3, the average being 0.27 electrons/Å^3.

The values of positional and thermal parameters for both complexes are presented in Tables 6 to 11. Observed and calculated structure factors for both sets of data are tabulated in Appendices I and II.

In the final stages of the refinements, the structure factors were weighted according to:

$$w = k/(\sigma^2(F) + |g|F^2)$$

where k was determined from refined values of g.

For mercury, the final values were $g = 0.006423$ and $k = 1.000$. The overall scale factor refined to 1.491 (±0.005). The equivalent figures for the cadmium structure were $g = 0.009458$ and $k = 1.000$, with an overall scale factor of 1.647 (±0.005).

Table 6. Positional Parameters for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses

$HgCl_2 \cdot$18-Crown-6	Values x 10^4		
	x/a	y/b	z/c
*Hg1	0	0	0
Cl(1)	-1908(2)	-4.5(2)	1910(3)
O(1)	1314(6)	1464(6)	2106(8)
O(2)	1133(6)	-973(6)	2798(8)
O(3)	-337(6)	2438(6)	-164(9)
C(1)	574(9)	3089(8)	636(15)
C(2)	687(10)	2567(8)	2393(14)
C(3)	1582(10)	929(9)	3664(12)
C(4)	2122(9)	-250(10)	3264(12)
C(5)	1512(9)	-2146(9)	2526(13)
C(6)	454(10)	-2819(9)	1812(13)

* Position fixed by symmetry.

Table 7. Anisotropic Thermal Parameters† for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses (Vibrational-tensor components $Å^2$)

$HgCl_2 \cdot$18-Crown-6

Values are x 10^4

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg(1)	342(3)	394(3)	450(3)	9(2)	-57(2)	-9(2)
Cl(1)	423(10)	610(12)	566(11)	20(9)	24(8)	-7(9)
O(1)	502(32)	560(33)	470(28)	4(24)	-49(24)	-35(26)
O(2)	423(29)	570(34)	571(32)	12(26)	-72(24)	59(25)
O(3)	469(31)	500(32)	617(34)	50(26)	-44(26)	-52(26)
C(1)	518(49)	367(38)	842(62)	-14(37)	-90(43)	-68(35)
C(2)	595(51)	476(45)	698(54)	-165(38)	-111(42)	-38(39)
C(3)	630(55)	668(56)	516(45)	-6(39)	-189(40)	-98(45)
C(4)	476(46)	819(64)	482(41)	74(40)	-155(35)	9(44)
C(5)	561(50)	607(52)	584(47)	81(39)	-122(39)	155(42)
C(6)	589(52)	501(46)	649(51)	109(38)	-58(40)	44(40)

† Anisotropic temperature factors are given by:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{12}hka^*b^*\cos\gamma^* + 2U_{13}h\ell a^*c^*\cos\beta^* + 2U_{23}k\ell b^*c^*\cos\alpha^*)]$$

Table 8. Positional and Isotropic† Thermal Parameters for Hydrogen Atoms (calculated assuming local C_{2v} symmetry of the methylene groups with C-H = 1.0 Å, H-C-H = 109°).

$HgCl_2 \cdot$ 18-Crown-6

Values are x 10^4

Atom	x/a	y/b	z/c	U†
H(1)	1501	3051	-169	783
H(2)	264	3987	787	783
H(3)	-264	2452	3116	783
H(4)	1251	3130	3112	783
H(5)	2274	1448	4240	783
H(6)	700	861	4563	783
H(7)	2480	-604	4398	783
H(8)	2903	-201	2199	783
H(9)	2363	-2183	1565	783
H(10)	1730	-2517	3734	783
H(11)	-476	-2646	2763	783
H(12)	623	-3728	1838	783

† Isotropic temperature factors are given by:

$\exp[-8\pi^2 U \sin\theta^2/\lambda^2]$.

The hydrogen atoms H1, H2 are bonded to C1; H3, H4 to C2 etc.

Table 9. Positional Parameters for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses

$CdCl_2 \cdot$18-Crown-6	Values x 10^4		
	x/a	y/b	z/c
*Cd1	0	0	0
Cl1	-1971(1)	-0.3(1)	1966(1)
O(1)	1240(2)	1449(2)	2086(3)
O(2)	1146(2)	-942(2)	2687(3)
O(3)	-295(2)	2385(2)	-210(3)
C(1)	572(3)	3093(2)	631(4)
C(2)	667(3)	2563(2)	2362(4)
C(3)	1584(3)	949(3)	3651(4)
C(4)	2136(3)	-231(3)	3223(4)
C(5)	1520(3)	-2145(3)	2522(4)
C(6)	420(3)	-2805(2)	1881(4)

* Position fixed by symmetry.

Table 10. Anisotropic Thermal Parameters† for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses (Vibrational tensor components $Å^2$).

$CdCl_2 \cdot$18-Crown-6

Values are x 10^4

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cd1	392(3)	486(3)	366(3)	2(2)	25(2)	-12(2)
Cl1	425(5)	543(5)	421(5)	1(3)	44(4)	-13(3)
O(1)	586(12)	437(9)	327(9)	-13(7)	-62(8)	-22(8)
O(2)	450(10)	507(10)	443(11)	-28(8)	-77(8)	52(7)
O(3)	451(10)	435(9)	481(11)	33(8)	-62(8)	-86(7)
C(1)	572(17)	430(13)	544(17)	-24(12)	-99(13)	-101(11)
C(2)	628(17)	427(13)	465(16)	-72(11)	-102(12)	-24(11)
C(3)	572(17)	631(16)	324(13)	-61(12)	-94(11)	-52(13)
C(4)	502(15)	663(17)	465(16)	2(13)	-174(12)	-9(13)
C(5)	543(2)	485(14)	522(16)	34(12)	-110(13)	116(12)
C(6)	643(17)	434(13)	533(17)	103(12)	-67(13)	-0.2(13)

† see page 45.

Table 11. Positional and Isotropic† Thermal Parameters for Hydrogen Atoms (calculated assuming local C_{2v} symmetry of the Methylene Groups with C-H = 1.0 Å, H-C-H = 109°).

$CdCl_2 \cdot$18-Crown-6

Values are x 10^4

Atom	x/a	y/b	z/c	U†
H(1)	1519	3109	-155	609
H(2)	198	3974	798	609
H(3)	-292	2480	3103	609
H(4)	1264	3108	3069	609
H(5)	2298	1492	4152	609
H(6)	728	878	4619	609
H(7)	2464	-611	4365	609
H(8)	2946	-165	2183	609
H(9)	2393	-2233	1589	609
H(10)	1694	-2483	3773	609
H(11)	-475	-2640	2768	609
H(12)	623	-3729	1861	609

† see page 46.

Section 4 Results and Discussion

The structures of $HgCl_2$·18-crown-6 and $CdCl_2$·18-crown-6 are virtually identical. The structure of the $HgCl_2$ complex with the numbering scheme for the atoms of both complexes is shown in Figure 9. The view depicted is a projection on the yz plane, with a rotation of 5° about y to avoid overlap of the Cl-Hg-Cl system.

The Hg(1) atom lies at the origin (0,0,0) with the second Hg atom, related to the first by a C-face centring operation, at ($\frac{1}{2}$,$\frac{1}{2}$,0). Both atoms are located at centres of inversion.

Each mercury atom is chelated by a single molecule of 18-crown-6 via the 6 oxygen donor atoms. The oxygen atoms and the metal ion lie in a plane, with hexagonal bipyramidal coordination being completed by two chloride ions above and below the plane of the ring. The structure of the molecule is of the type illustrated in Figure 3(i) and Figure 4(top).

The details of the structure of the molecule, the coordination polyhedron and the packing of the molecules are discussed in greater detail in the following subsections.

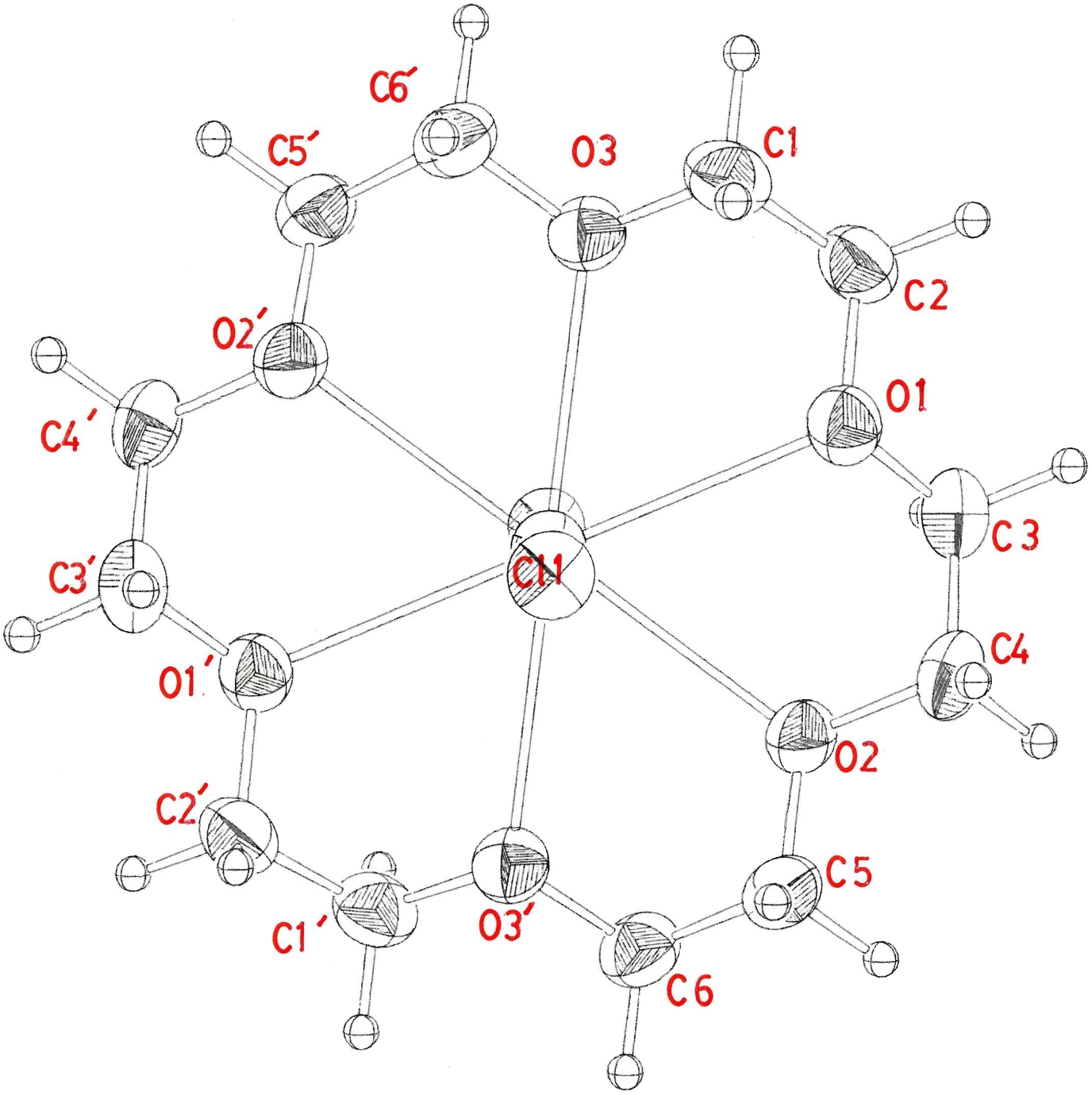


FIG 9 NUMBERING SCHEME

A. The $HgCl_2$·18-Crown-6 Molecule

Figure 10 depicts a molecule of the complex viewed from the side. The bond lengths and angles together with their estimated standard deviations are given in Tables 12 and 14, for both complexes. For comparison, Table 13 gives the details of the same distances and angles for the complex KNCS·18-Crown-6 (18).

For the $HgCl_2$ complex the equation of the mean plane through the O atoms is:

$$0.77307x - 0.00160y - 0.63432z = 0.0000$$

The Hg^{2+} ion lies in the mean plane of the 6 oxygen atoms. This was also found to be true for the $CdCl_2$ complex. The perpendicular distances to this plane for the atoms defining the plane and for the other atoms of the macrocyclic ring are presented in Table 14. The average C-C bond length in the ring is 1.493 Å. Given the average e.s.d. of 16, this is within the average value quoted in (61) for C-C bond lengths. The average C-O bond length is 1.417 Å which, again, compares well with the average value of 1.410 Å from (61).

Comparison of the Hg-Cl and CdCl bond-distances indicated, that on changing from Cd^{2+} to Hg^{2+}, the metal-chloride bond decreases in length. The metal-oxygen bonds, under the same circumstances, increase in length. As judged by the $O\text{-}O^i$ distances, ring expansion occurs on changing from Cd^{2+} to Hg^{2+}. This is consistent with the larger ionic radius of Hg^{2+}. (rHg^{2+} = 1.10 Å; rCd^{2+} = 0.97 Å; 62)

The softer (b)-acceptor Hg^{2+} would be expected to interact more strongly with the soft base Cl^-, resulting in a shorter $Hg^{2+}\text{-}Cl^-$ bond

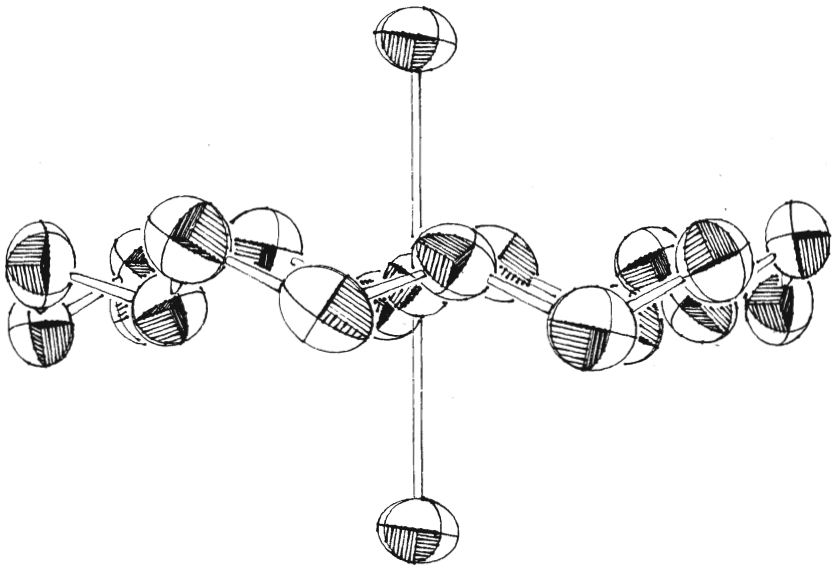


Figure 10. Side view of molecule of $HgCl_2$ complex.

Table 12. Bond Distances (Å), Bond Angles (°) and Torsion Angles (°) in the Centrosymmetric 18-Membered Ring

Atoms	$HgCl_2$·18-Crown-6			$CdCl_2$·18-Crown-6		
1 2 3 4	Distance 2-3	Angle 1-2-3	Torsion Angle 1-2-3-4	Distance 2-3	Angle 1-2-3	Torsion Angle 1-2-3-4
C6'-O3 -C1-C2	1.418(12)		-176	1.432(3)		-178.5
O3 -C1-C2-O1	1.507(16)	109.0(0.7)	-69.7	1.483(4)	107.8(0.2)	-64.0
C1-C2-O1-C3	1.426(12)	107.5(0.8)	174.7	1.408(4)	108.1(0.2)	169.8
C2-O1-C3-C4	1.416(11)	112.9(0.7)	175	1.428(3)	112.5(0.2)	178.2
O1-C3-C4-O2	1.482(16)	109.3(0.8)	70.0	1.483(4)	108.0(0.2)	64.1
C3-C4-O2-C5	1.410(12)	108.6(0.8)	-175	1416(4)	108.3(0.2)	-170.4
C4-O2-C5-C6	1.410(12)	113.5(0.7)	-174.8	1429(3)	112.2(0.2)	-177.8
O2-C5-C6-O3'	1.490(15)	109.8(0.8)	-69.1	1.509(5)	107.5(0.2)	-64.0
C5-C6-O3'-C1'	1.422	109.4(0.8)	-175.1	1.398	107.9(0.2)	-170.0

Table 13. Bond Distances (Å), Bond Angles (°) and Torsion Angles (°) in KNCS•18-Crown-6 (18).
The numbering shceme used in the original paper has been altered to correspond to that used in this work.

Atoms	Distance	Angle	Torsion Angle
1 2 3 4	2-3	1-2-3	1-2-3-4
C6'-O3-C1-C2	1.418	112.9	-170.8
O3-C1-C2-O1	1.497	108.1	-65.2
C1-C2-O1-C3	1.414	108.9	178.9
C2-O1-C3-C4	1.418	111.6	178.1
O1-C3-C4-O2	1.507	108.2	70.0
C3-C4-O2-C5	1.418	109.4	-175.5
C4-O2-C5-C6	1.417	112.0	-177.4
O2-C5-C6-O3'	1.507	108.9	-65.3
C5-C6-O3'-C1'	1.424	107.5	-177.5

Table 14. Distances (Å) for each complex involving the metal and chloride ions.

(e.s.d. in parentheses)

Hg-O(1)	2.826(6)	Cd-O(1)	2.754(2)
Hg-O(2)	2.835(6)	Cd-O(2)	2.753(2)
Hg-O(3)	2.822(7)	Cd-O(3)	2.747(2)
Hg-Cl	2.316(2)	Cd-Cl	2.369(1)

For comparison, the average metal-oxygen and metal-chloride bond lengths found in typical compounds are:

Hg-O	2.49(5) Å (average of values in Table 3)
Cd-O	2.346(2) Å
Hg-Cl	2.27(3) Å in $HgCl_2$
Cd-Cl	2.23(3) Å in $CdCl_2$

Table 15. Perpendicular distances to least squares plane defined by six oxygen atoms.

Atom	Perpendicular distance to plant
OX1	-0.15627
OX2	0.15615
OX3	0.15664
OX1'	0.15627
OX2'	-0.15615
OX3'	-0.15664

(compared to Cd^{2+}-Cl^{-}) and a weakening of the Hg^{2+}-O bond (compared to Cd^{2+}-O).

This behaviour may be compared to the Cd and Hg compounds described in (55). Comparing these together (refer to Table 3; 55) the main differences between the two structures are:

(i) a decrease in the metal-iodide distance,

(ii) an increase in the metal-oxygen and metal-nitrogen distances when the central ion changes from Cd^{2+} to Hg^{2+},

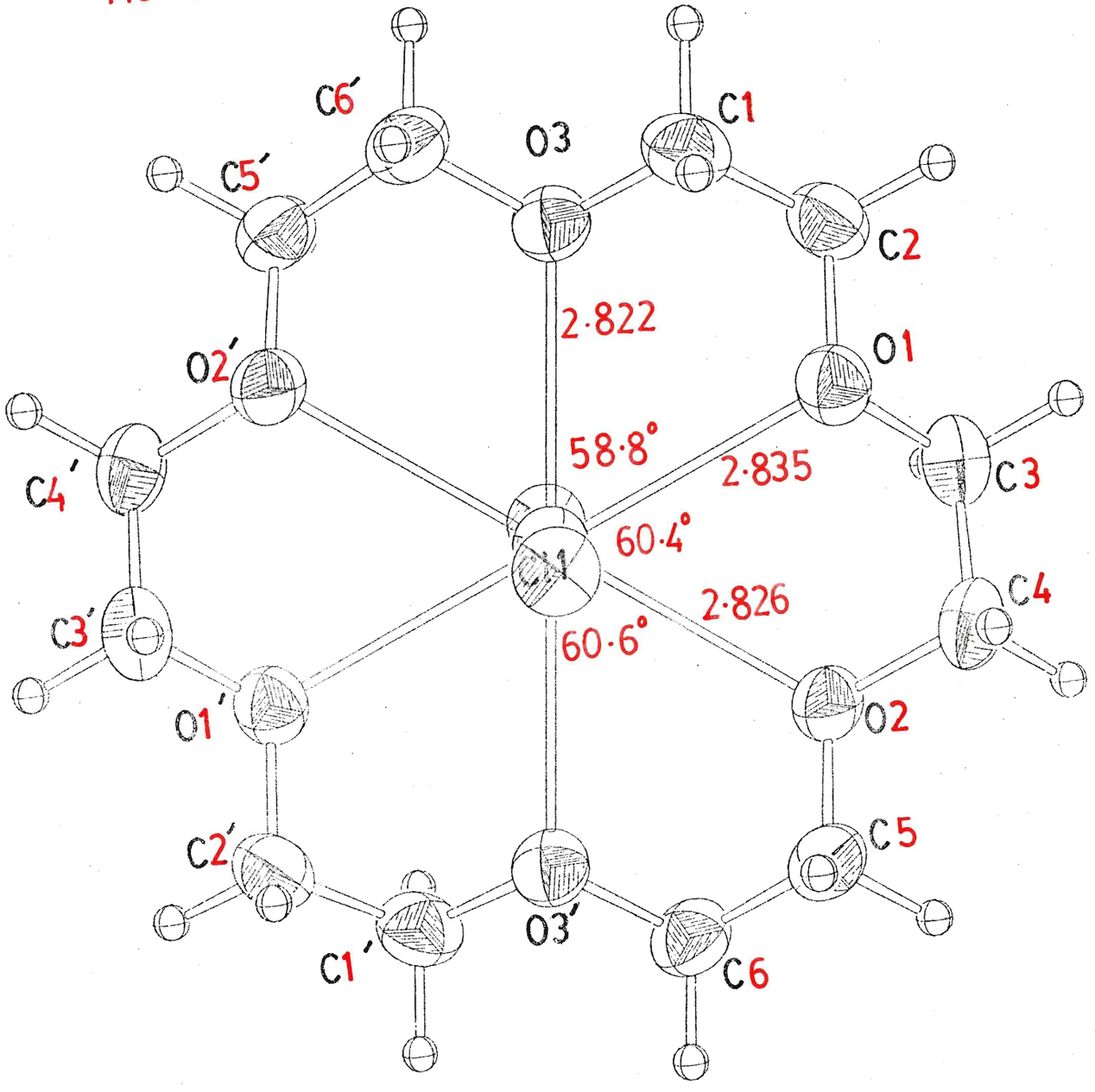
(iii) ring expansion on changing from Cd^{2+} to the larger Hg^{2+}, as indicated by the change in $O\text{-}O_i$ distances (O_i is the symmetry related oxygen atom in the macrocyclic ring, generated by the action of the inversion centre at the metal ion). This expansion is as expected.

Formation constant studies in aqueous solutions (55) indicate similar strength interactions between the weak (b)-acceptor Cd^{2+} and both N and I^{-} With the stronger (b)-acceptor Hg^{2+} there is a much stronger Hg^{2+}-I^{-} interaction. Thus, the large $N\text{-}N_i$ expansion on going from Cd^{2+} to Hg^{2+} must be related to the very strong linear I^{-}-Hg^{2+}-I^{-} interaction which consequently weakens the Hg^{2+}-N interaction. The similar affinities of Cd^{2+} for N and I^{-} result in the Cd-I distance being longer than that found in CdI_2 itself (2.60 Å (62)).

The distances and angles for the $HgCl_2$·18-Crown-6 structure may also be compared to those observed in (50) for the complex of $HgCl_2$ with tetraethylene glycol dimethyl ether (TGM), this comparison being done in Figure 11a,b. In this Figure, the numbering scheme used for the atoms is that presented in the original paper.

FIG 11a $HgCl_2$ 18CROWN 6

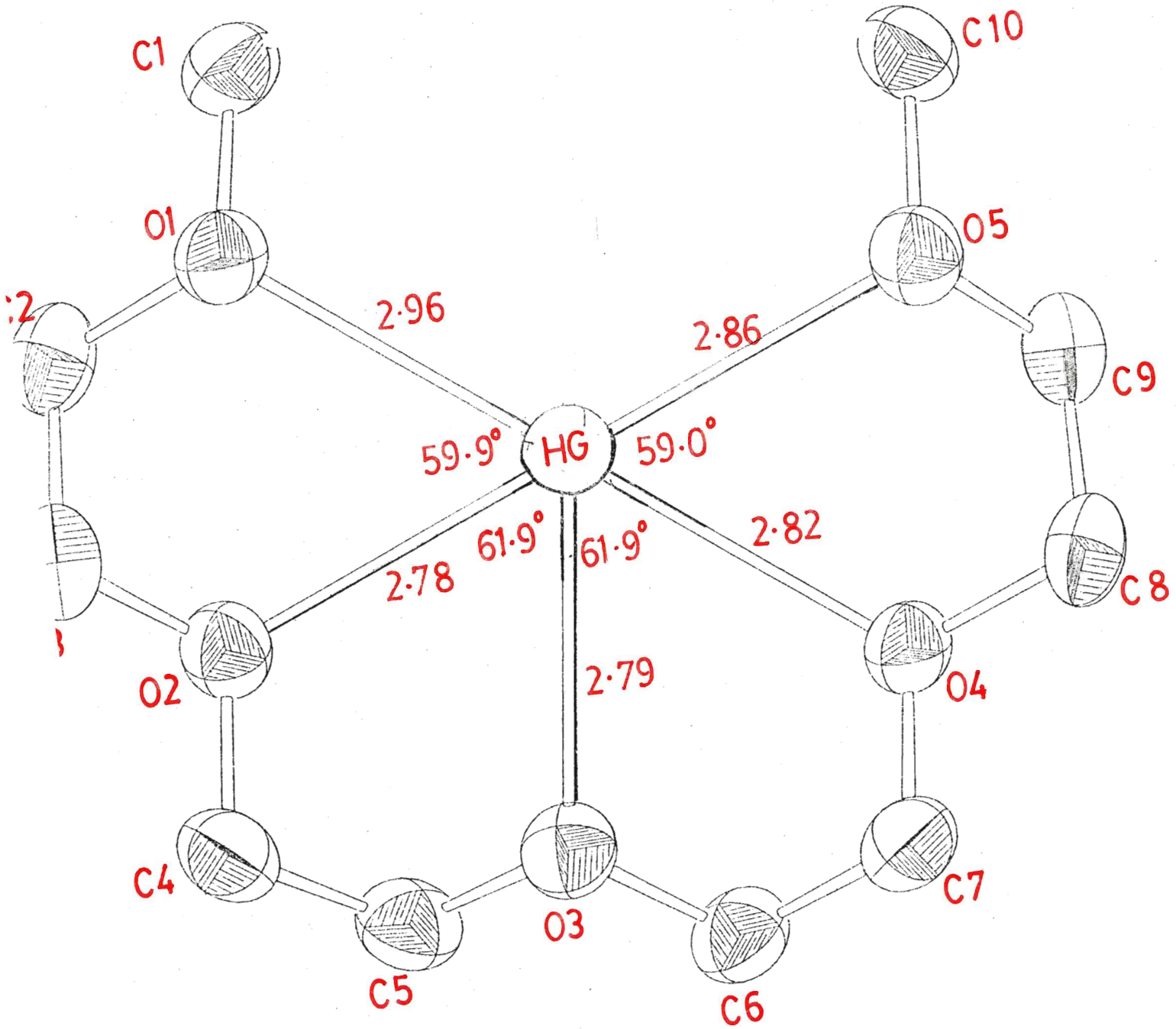
HG-O interactions



HG-Cl = 2·316 Å

FIG 11b $HGCl_2$.TGM

HG-O interactions



HG-Cl=2·291-2·311Å

A comparison of the torsion angles of the $HgCl_2$•18-crown-6 and $CdCl_2$•18-crown-6 complexes with those for a similar complex, namely KNCS•18-crown-6 (18) shows that all the torsion angles are comparable (Tables 12, 13). The magnitude of the average O-C-C-O torsion angle for the Hg(II) complex is 69.6°, while that for the Cd(II) complex is 64.0°. For comparison, the equivalent value for KNCS•18-crown-6 is 66.8°, while it has been stated earlier that values near 60° are indicative of a low level of torsional strain.

Similarly, a comparison may be made between the C-C-O-C torsion angles for the same three complexes. The average C-C-O-C torsion angle for the Hg(II) complex is 175.1°, for the Cd(II) complex is 174.1° and for the KNCS complex is 176.4°. The accepted value for a low level of torsional strain is 180°. Clearly the structure in both of the present complexes exhibits a low level of torsional strain and is closely related to similar structures described in the literature.

B.

Copies of ^{1}H and ^{13}C NMR spectra are in Appendix IV. The spectra are similar for the uncomplexed crown and both of the complexes.

The ^{1}H NMR spectrum shows a strong resonance at 3.70 ppm for the 18-crown-6 and for the $HgCl_2$•18-crown-6 complex. The $CdCl_2$•18-crown-6 shows the same type of absorption at δ = 3.83 ppm. No other features are in evidence apart from spinning side-bands and chloroform impurity absorption. The resonance observed for the crown and each of the complexes was not perfectly sharp, probably due to the presence of an impurity in the sample.

The ^{13}C spectra for the uncomplexed crown and the ($CdCl_2$•complex) show a single sharp resonance at δ = 70.72 ppm and 69.81 ppm respectively. The ($HgCl_2$•complex) spectrum shows a single absorption at 70.18. The spectra indicate that all the ring carbon atoms are equivalent.

The initial ^{13}C spectrum for the $HgCl_2$•18-crown-6 exhibited 2 peaks, one at 70.18 ppm and the other, at 70.72 ppm, corresponding to uncomplexed crown. It was initially believed that this could be due to decomposition, in $CDCl_3$, of the complex. When the spectrum was re-run with $HgCl_2$•18-crown-6 that had been left for some weeks, the absorption due to uncomplexed 18-crown-6 was absent; only a single sharp resonance at 70.18 ppm being observed.

When a small amount of 18-crown-6 was added to this sample of the complex, and the ^{13}C spectrum was re-run, an absorption appeared at 70.72 ppm indicating that the original absorption at this frequency was due to uncomplexed crown present in the original sample, and not decomposition of the complex. Thus the Hg-O interactions are strong ones.

From the ^{13}C NMR, it seems that the complexes absorb to low-field of the uncomplexed crown. It would seem reasonable to infer that this could be due to removal of electron density from the region of the carbon atoms, associated with the involvement of the oxygen atoms in bond formation with the metal ions. However, this line of reasoning cannot account for the relative chemical shifts of the complexes. It is known that the metal ion-induced shifts are small changes superimposed on other effects involving solvent and pH (63). Even so, the shifts of Cd and Hg relative to free ligand are suggestive.

The mass spectral data summarized in Table 16 indicate that Hg and Cd are present in the respective complexes. A reasonable fragmentation scheme to account for the fragmentation patterns of both the crown and the complexes is outlined in Figure 12.

Most reports in the literature seem to give only the molecular compositions (64), and details of the fragmentation patterns do not seem to be available at the time of writing. The structural identities of the $C_2H_4O^+$ species lost are uncertain. They could be open-chain species as drawn, or ring closure concomitant with bond cleavage could occur. Throughout, it has been assumed that elemental compositions of fragment ions, of 18-crown-6 and both the complexes, that are isobaric, are identical.

Table 16. Major Peaks in the Mass Spectra of 18-Crown-6, $HgCl_2$·18-Crown-6 and $CdCl_2$·18-Crown 6
Electron impact; solid probe 4 kV accelerating voltage.

18-Crown-6 (I) Fragment	m/e (%)	$HgCl_2$·18-Crown-6 (II)	m/e (%)	$CdCl_2$·18-Crown-6 (III)	m/e (%)
		Hg^+	202 (8)	Cd^+	110-116 (6.5)
$C_8H_{17}O_4^+$	177 (1.6)		177 (1.1)		177 (2.6)
$C_6H_{13}O_3^+$	133 (8.8)		133 (6.8)		133 (6.5)
$C_6H_{13}O_2^+$	117 (3.4)		117 (2.8)		117 (5.2)
$C_6H_{13}O^+$	101 (2.3)		101 (7.2)		101 (9.2)
$C_4H_9O_2^+$	89 (40.7)		89 (34.4)		89 (50.8)
$C_4H_9O^+$	73 (23.1)		73 (19.4)		73 (26.7
$C_3H_7O^+$	59 (18.1)		59 (16.7)		59 (18.8)
$C_3H_6O^+$	58 (17.3)		58 (16.4)		58 (19.4)
$C_2H_5O^+$	45 (100)		45 (100)		45 (100)
No M^+ ion		No M^+ ion		No M^+ ion	

The % intensity data are with respect to the base peak. Codes I, II, III are used to refer to spectra in Appendix IV.

Figure 12. A hypothetical fragmentation scheme to account for the peaks in the mass spectrum of 18-Crown-6.

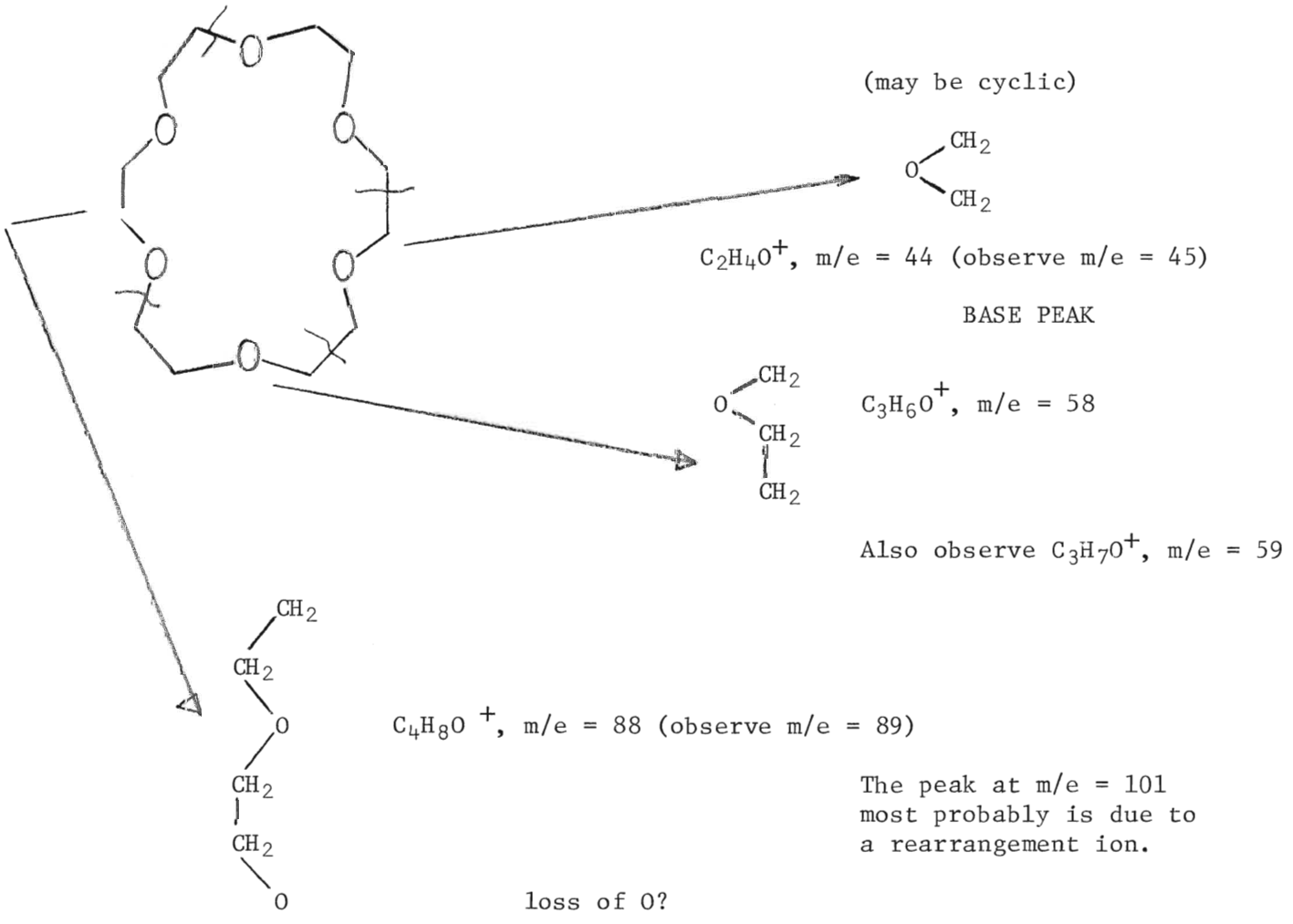
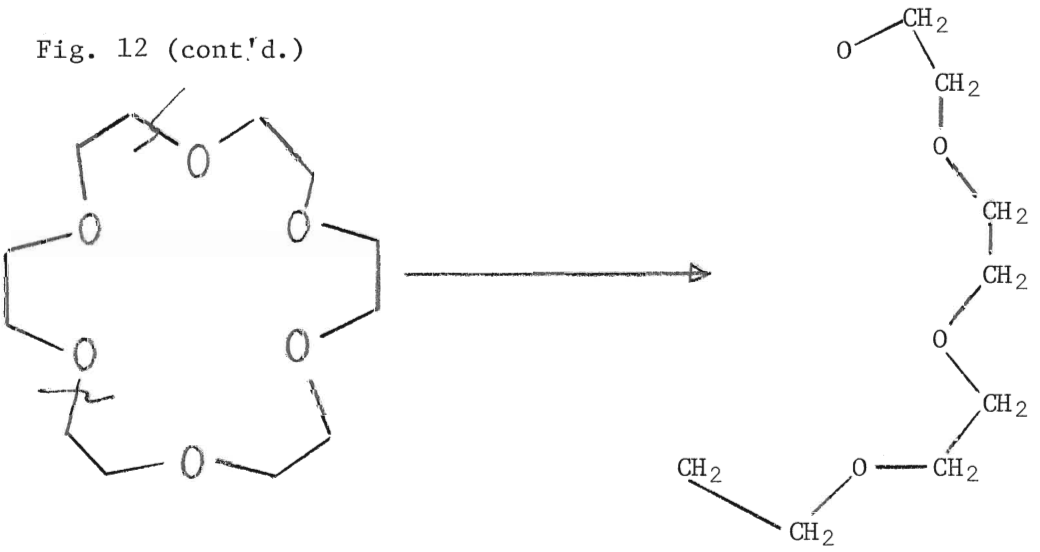
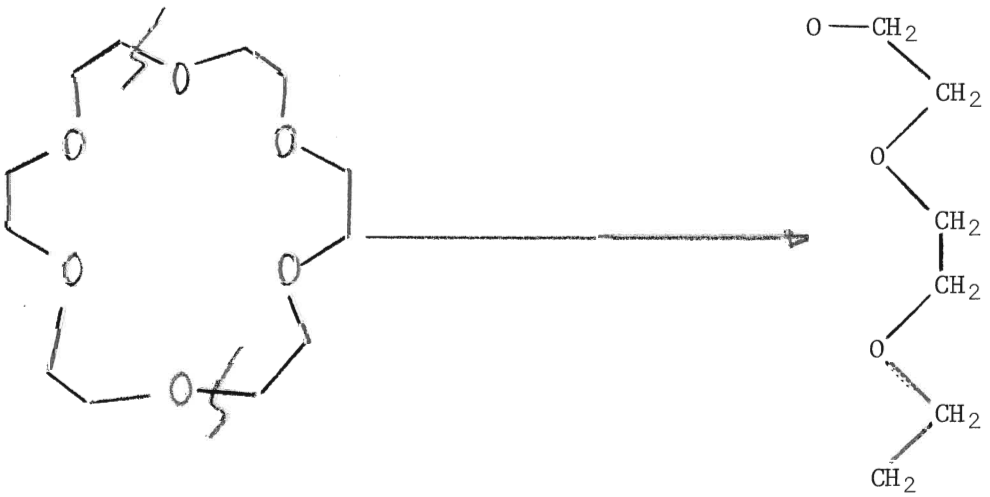


Fig. 12 (cont'd.)



$C_8H_{16}O_4^+$, m/e = 176

(observe m/e = 177)



$C_6H_{12}O_3^+$, m/e = 132

(observe m/e = 133)

loss of terminal O?

$C_6H_{13}O_2^+$, m/e = 117

C. The Metal Coordination

Figure 13 is a stereoscopic view of the coordination polyhedron of the metal atom in both complexes. This is clearly a hexagonal bipyramid, the metal ion and oxygen atoms being in a plane, with the two chloride ions forming a linear system along the axis. Table 17 shows the polyhedral angles.

Clearly the complexes are of the type described in the Introduction as Figure 3(i) and Figure 4, with the metal ion in the ligand cavity, complexed by ion-dipole interaction with all the oxygen donor atoms. The metal-oxygen bond lengths compared to those in (55) are a little longer consistent with the involvement of Hg^{2+} in interactions with another ligand, namely N, in the diaza-crown complex.

As stated earlier, the hexagonal bipyramidal coordination for either Hg(II) or Cd(II) is extremely rare and not particularly favourable. A tentative explanation for this unusual geometry is as follows. Firstly, the conformations of 18-crown-6 found in its complexes with KNCS, RbNCS and CsNCS have approximate D_{3d} symmetry (18). All torsion angles about C-C bonds are close to 65°, and those about C-O bonds are close to 180°. In all three of these structures, the six oxygen atoms are alternately approximately 0.20 Å above and below the least squares plane, thus forming a nearly planar hexagon of side about 2.80 Å.

It is an important property of the hexaether than nearly optimal values of all the parameters required for strict D_{3d} symmetry can be attained simultaneously, which may explain the essential invariance of the observed ring conformation in complexes of the present type.

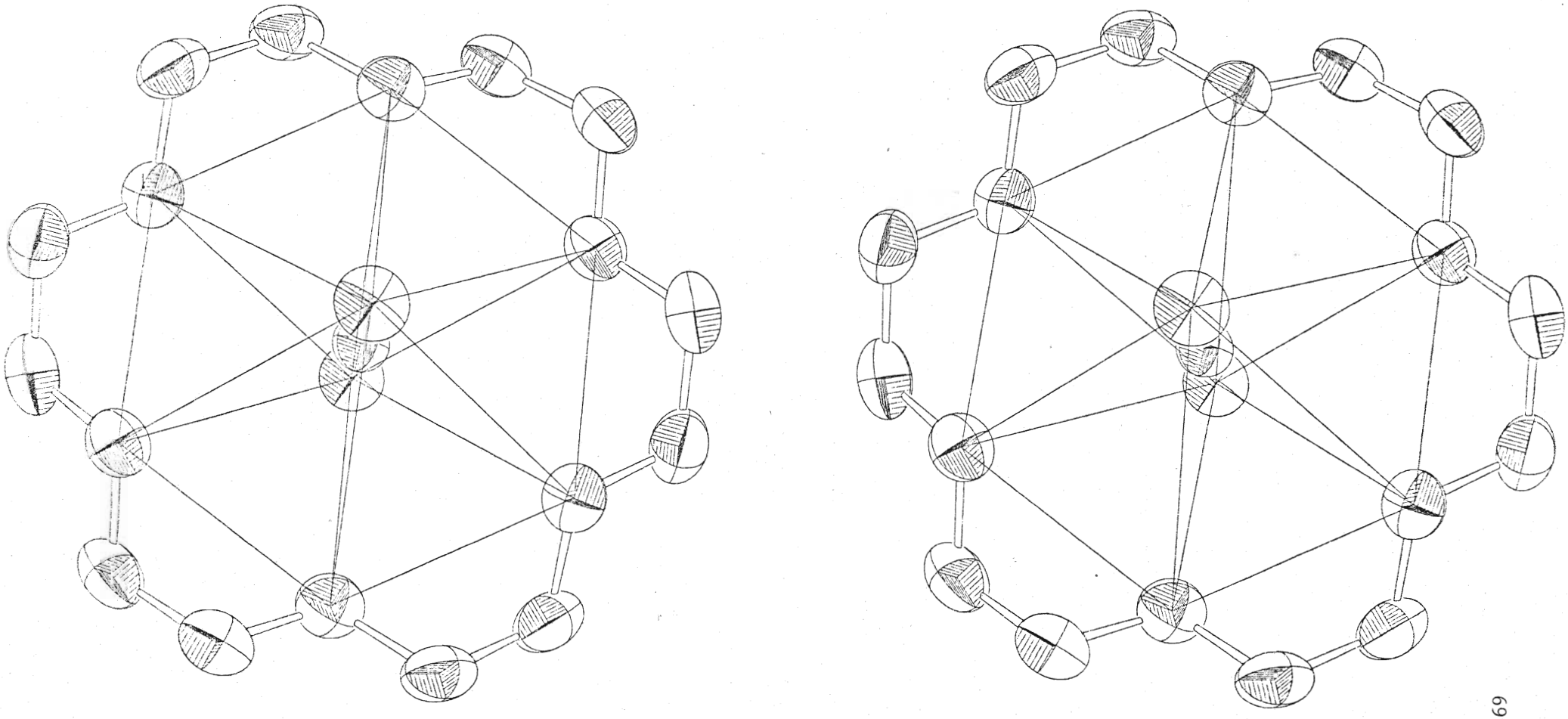


Figure 13. Coordination polyhedron of $HgCl_2$ complex.

Secondly, the removal of the linearity of the Cl-Hg-Cl system (i.e., a "bent" Cl-Hg-Cl system) would have the effect of bringing ligating species of the same sign closer towards one another. Thus, the $HgCl_2$ and $CdCl_2$-18-crown-6 complexes probably exhibit the (puckered) hexagonal bipyramidal coordination (rather than the more common square antiprismatic or dodecahedral forms) as a requirement to maintain the nearly optimal values for the torsion angles, bond distances and angles associated with the macrocyclic ring (i.e., to minimise conformational strain) and in order to minimise electrostatic interaction between Cl^- and the oxygen atoms.

Table 17. Angles associated with the coordination polyhedron.

$Cl-Hg-O_1$	94.3° (0.1)
$Cl-Hg-O_2$	85.5° (0.1)
$Cl-Hg-O_3$	86.0° (0.1)
O_1-Hg-O_2	60.4° (0.2)
O_1-Hg-O_3	58.8° (0.2)
$O_3'-Hg-O_2$	60.6° (0.2)
$Cl-Cd-O_1$	93.2° (0.0)
$Cl-Cd-O_2$	86.7° (0.0)
$Cl-Cd-O_3$	86.8° (0.0)
O_1-Cd-O_2	60.4° (0.1)
O_1-Cd-O_3	60.2° (0.1)
$O_3'-Cd-O_2$	60.3° (0.1)

D. Molecular Packing

Figure 14 is a stereoscopic view of the packing of the complexes, with two molecules per unit cell. The view is on the crystallographic xz plane with rotations of 25° about y and 10° about x. The most striking feature of this perspective is the aligned Cl^{-}-Hg^{2+}-Cl^{-} systems, with their axes parallel to one another. While the space group demands this, it seems reasonable to conclude that such an arrangement minimises the electrostatic force of interaction of these systems of charges. The polyether rings, each being perpendicular to the Cl-Hg-Cl system, then form interleaving parallel sheets.

There is no evidence of hydrogen bonding in the molecules, nor any evidence for contacts less than the sum of Van der Waal's radii for any pairs of molecules. Typical distances between atoms in different molecules are: O-Cl $\geqslant$ 3.517 Å, O-H $\geqslant$ 3.328 Å, Cl-H $\geqslant$ 3.311 Å. The Van der Waals radii used were O = 1.40 Å, H = 1.2 Å, Cl = 1.80 Å, $-CH_2$ = 2.0 Å (62); Hg = 1.73 Å (65).

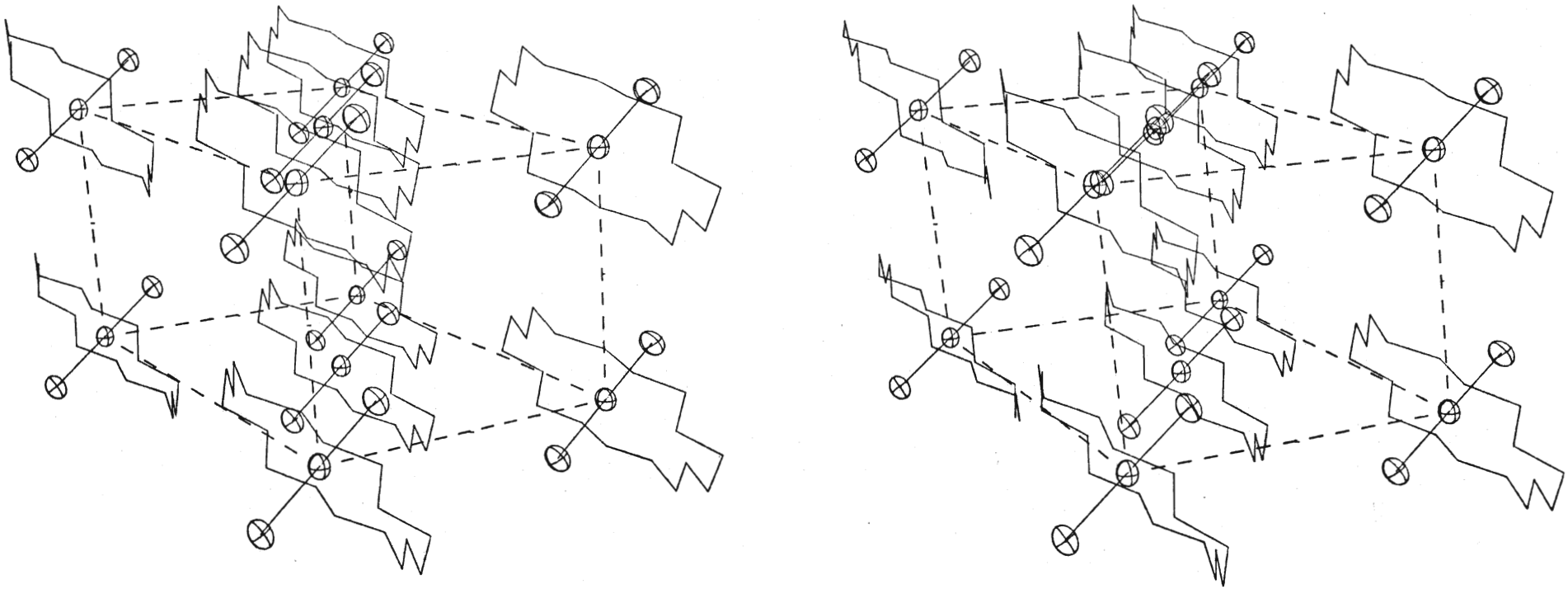


Figure 14. Stereoscopic view of packing of $HgCl_2 \cdot$18-Crown-6 molecules. (a is horizontal, c vertical.)

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Appendix I. Structure factor table for $HgCl_2 \cdot$18-Crown-6

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
2	0	0	1281	1326	-1	3	0	1737	1620	2	6	0	801	736	-4	10	0	510	477	1	-11	1	468	443
4	0	0	1050	961	1	3	0	1596	1457	4	6	0	845	789	-2	10	0	386	399	3	-11	1	411	383
6	0	0	1194	1115	3	3	0	1207	1104	6	6	0	818	782	0	10	0	728	680	5	-11	1	420	391
8	0	0	521	501	5	3	0	1550	1434	8	6	0	433	430	2	10	0	446	415	7	-11	1	370	346
10	0	0	519	521	7	3	0	271	264	10	6	0	453	476	4	10	0	415	404	-8	-10	1	274	280
12	0	0	242	247	9	3	0	366	361	-9	7	0	430	409	6	10	0	463	451	-6	-10	1	293	285
-11	1	0	402	415	11	3	0	449	479	-7	7	0	416	395	8	10	0	238	239	-4	-10	1	580	560
-9	1	0	568	562	-10	4	0	417	420	-5	7	0	901	841	-7	11	0	291	271	-2	-10	1	458	439
-7	1	0	699	670	-8	4	0	381	377	-3	7	0	885	796	-5	11	0	467	446	0	-10	1	544	524
-5	1	0	1295	1232	-6	4	0	1078	984	-1	7	0	893	1030	-3	11	0	350	316	2	-10	1	644	595
-3	1	0	458	429	-4	4	0	1500	1369	1	7	0	1078	1000	-1	11	0	430	433	4	-10	1	429	393
-1	1	0	1793	2028	-2	4	0	1186	1097	3	7	0	506	484	1	11	0	575	533	6	-10	1	468	448
1	1	0	1827	2018	0	4	0	2087	1893	5	7	0	807	766	3	11	0	364	345	8	-10	1	250	245
3	1	0	322	297	2	4	0	1181	1051	7	7	0	420	410	5	11	0	409	401	-7	-9	1	340	341
5	1	0	1545	1430	4	4	0	1507	1392	9	7	0	325	330	7	11	0	231	239	-5	-9	1	547	529
7	1	0	898	838	6	4	0	904	861	-8	8	0	340	322	-4	12	0	314	303	-3	-9	1	657	637
9	1	0	712	696	8	4	0	247	239	-6	8	0	509	479	-2	12	0	254	285	-1	-9	1	621	598
11	1	0	518	536	10	4	0	549	566	-4	8	0	719	668	0	12	0	509	483	1	-9	1	834	804
-12	2	0	291	294	-11	5	0	366	368	-2	8	0	821	769	2	12	0	404	381	3	-9	1	442	413
-10	2	0	706	692	-9	5	0	380	368	0	8	0	1172	1071	4	12	0	348	352	5	-9	1	475	436
-8	2	0	646	627	-7	5	0	531	520	2	8	0	542	507	-3	13	0	246	237	7	-9	1	502	481
-6	2	0	1087	1018	-5	5	0	1332	1207	4	8	0	657	624	-1	13	0	350	357	9	-9	1	233	230
-4	2	0	1094	1014	-3	5	0	683	648	6	8	0	749	712	1	13	0	382	358	-8	-8	1	426	429
-2	2	0	330	310	-1	5	0	594	635	8	8	0	336	337	3	13	0	247	237	-6	-8	1	454	438
0	2	0	1326	1238	1	5	0	1286	1194	-9	9	0	318	302	-3	-13	1	333	331	-4	-8	1	722	706
2	2	0	327	312	3	5	0	893	816	-7	9	0	327	315	-1	-13	1	321	319	-2	-8	1	645	596
4	2	0	1383	1288	5	5	0	1325	1214	-5	9	0	544	521	1	-13	1	404	391	0	-8	1	996	926
6	2	0	1183	1110	7	5	0	645	611	-3	9	0	446	435	3	-13	1	271	260	2	-8	1	866	798
8	2	0	493	482	9	5	0	591	583	-1	9	0	685	721	-4	-12	1	445	446	4	-8	1	349	318
10	2	0	705	704	11	5	0	441	470	1	9	0	741	694	-2	-12	1	340	331	6	-8	1	739	685
12	2	0	323	338	-10	6	0	454	452	3	9	0	376	372	0	-12	1	376	347	8	-8	1	477	472
-11	3	0	423	437	-8	6	0	363	348	5	9	0	750	707	2	-12	1	384	367	10	-8	1	289	278
-9	3	0	611	593	-6	6	0	820	771	7	9	0	482	473	4	-12	1	299	273	-9	-7	1	442	449
-7	3	0	692	648	-4	6	0	1005	920	9	9	0	315	315	-5	-11	1	397	398	-7	-7	1	365	352
-5	3	0	1473	1320	-2	6	0	370	365	-8	10	0	253	237	-3	-11	1	467	449	-5	-7	1	666	628
-3	3	0	1217	1075	0	6	0	1047	998	-6	10	0	455	442	-1	-11	1	278	257	-3	-7	1	768	735

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-1	-7	1	764	711	4	-4	1	895	809	5	-1	1	1120	1046	4	2	1	999	925	5	5	1	1018	945
1	-7	1	1095	1247	6	-4	1	1013	946	7	-1	1	999	957	6	2	1	1227	1173	7	5	1	962	952
3	-7	1	680	622	8	-4	1	440	431	9	-1	1	352	347	8	2	1	758	756	9	5	1	479	491
5	-7	1	606	564	10	-4	1	390	384	11	-1	1	435	452	10	2	1	482	496	11	5	1	379	409
7	-7	1	757	712	-11	-3	1	250	269	-12	0	1	162	178	12	2	1	361	398	-10	6	1	406	406
9	-7	1	346	336	-9	-3	1	426	432	-10	0	1	550	575	-11	3	1	388	397	-8	6	1	479	449
-10	-6	1	446	462	-7	-3	1	625	613	-8	0	1	616	610	-9	3	1	664	653	-6	6	1	631	590
-8	-6	1	478	469	-5	-3	1	1412	1513	-6	0	1	675	654	-7	3	1	508	475	-4	6	1	720	679
-6	-6	1	530	507	-3	-3	1	1073	1006	-4	0	1	1836	1760	-5	3	1	1406	1296	-2	6	1	307	304
-4	-6	1	1007	945	-1	-3	1	1023	937	-2	0	1	2283	2621	-3	3	1	1344	1251	0	6	1	1228	1230
-2	-6	1	688	629	1	-3	1	1869	2026	0	0	1	1275	2019	-1	3	1	910	947	2	6	1	1078	980
0	-6	1	907	873	3	-3	1	1189	1088	2	0	1	1061	952	1	3	1	1862	1978	4	6	1	621	577
2	-6	1	1311	1148	5	-3	1	1101	996	4	0	1	955	899	3	3	1	1194	1089	6	6	1	895	878
4	-6	1	619	560	7	-3	1	1003	934	6	0	1	1389	1289	5	3	1	422	411	8	6	1	480	482
6	-6	1	808	759	9	-3	1	397	390	8	0	1	533	520	7	3	1	641	615	10	6	1	303	314
8	-6	1	464	437	11	-3	1	461	477	10	0	1	352	360	9	3	1	450	454	-9	7	1	439	422
10	-6	1	358	360	-10	-2	1	549	553	12	0	1	389	418	11	3	1	420	445	-7	7	1	434	406
-11	-5	1	348	357	-8	-2	1	612	595	-11	1	1	366	372	-10	4	1	467	467	-5	7	1	971	913
-9	-5	1	585	589	-6	-2	1	888	832	-9	1	1	701	678	-8	4	1	577	554	-3	7	1	893	853
-7	-5	1	549	542	-4	-2	1	1227	1138	-7	1	1	427	410	-6	4	1	918	859	-1	7	1	679	772
-5	-5	1	1051	990	-2	-2	1	448	410	-5	1	1	1015	961	-4	4	1	1521	1409	1	7	1	1076	986
-3	-5	1	1076	994	0	-2	1	395	934	-3	1	1	1521	1433	-2	4	1	928	904	3	7	1	528	466
-1	-5	1	655	604	2	-2	1	1666	1462	-1	1	1	1274	1384	0	4	1	1638	1732	5	7	1	595	569
1	-5	1	1318	1296	4	-2	1	885	813	1	1	1	1250	1229	2	4	1	1737	1600	7	7	1	502	494
3	-5	1	1051	939	6	-2	1	1339	1226	3	1	1	1076	1000	4	4	1	680	637	9	7	1	229	228
5	-5	1	833	768	8	-2	1	698	679	5	1	1	1510	1423	6	4	1	737	701	-8	8	1	317	307
7	-5	1	662	638	10	-2	1	447	443	7	1	1	1261	1198	8	4	1	591	569	-6	8	1	478	461
9	-5	1	321	311	12	-2	1	399	414	9	1	1	498	490	10	4	1	456	470	-4	8	1	970	926
11	-5	1	460	472	-11	-1	1	401	422	11	1	1	471	496	-11	5	1	240	245	-2	8	1	650	659
-10	-4	1	395	404	-9	-1	1	762	759	-10	2	1	693	681	-9	5	1	541	535	0	8	1	736	730
-8	-4	1	502	501	-7	-1	1	585	563	-8	2	1	537	513	-7	5	1	554	528	2	8	1	748	678
-6	-4	1	914	871	-5	-1	1	1065	1033	-6	2	1	584	538	-5	5	1	904	847	4	8	1	714	656
-4	-4	1	1438	1341	-3	-1	1	1526	1422	-4	2	1	1216	1122	-3	5	1	408	405	6	8	1	727	697
-2	-4	1	864	806	-1	-1	1	1363	1322	-2	2	1	301	297	-1	5	1	725	817	8	8	1	326	326
0	-4	1	1502	1461	1	-1	1	1275	1163	0	2	1	858	944	1	5	1	1762	1640	10	8	1	282	287
2	-4	1	1798	1610	3	-1	1	1049	913	2	2	1	1563	1614	3	5	1	1048	960	-7	9	1	220	211

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-5	9	1	518	501	-2	-12	2	295	297	8	-8	2	467	454	-4	-4	2	1035	989	-3	-1	2	1756	1740
-3	9	1	559	562	0	-12	2	305	292	-9	-7	2	364	412	-2	-4	2	1066	1038	-1	-1	2	269	310
-1	9	1	412	467	2	-12	2	387	443	-7	-7	2	356	360	0	-4	2	856	953	1	-1	2	1506	1624
1	9	1	690	655	4	-12	2	319	300	-5	-7	2	423	414	2	-4	2	1717	1640	3	-1	2	1576	1467
3	9	1	654	614	-5	-11	2	301	297	-3	-7	2	930	900	4	-4	2	823	738	5	-1	2	701	665
5	9	1	793	747	-3	-11	2	346	341	-1	-7	2	668	630	6	-4	2	790	745	7	-1	2	968	922
7	9	1	494	493	-1	-11	2	201	201	1	-7	2	720	822	8	-4	2	718	693	9	-1	2	448	434
9	9	1	252	252	1	-11	2	491	499	3	-7	2	713	662	10	-4	2	425	421	11	-1	2	371	396
-8	10	1	290	259	3	-11	2	497	474	5	-7	2	719	664	-11	-3	2	143	153	-10	0	2	373	382
-6	10	1	321	319	5	-11	2	319	303	7	-7	2	751	702	-9	-3	2	617	631	-8	0	2	716	728
-4	10	1	544	532	7	-11	2	379	369	9	-7	2	296	290	-7	-3	2	726	724	-6	0	2	669	642
-2	10	1	348	385	-6	-10	2	276	290	-10	-6	2	292	305	-5	-3	2	570	531	-4	0	2	1952	1943
0	10	1	568	548	-4	-10	2	529	520	-8	-6	2	517	537	-3	-3	2	1231	1191	-2	0	2	1390	1419
2	10	1	503	461	-2	-10	2	433	441	-6	-6	2	365	376	-1	-3	2	863	876	0	0	2	240	301
4	10	1	411	390	0	-10	2	467	445	-4	-6	2	950	920	1	-3	2	1599	1719	2	0	2	1828	2031
6	10	1	456	451	2	-10	2	626	644	-2	-6	2	954	893	3	-3	2	1331	1198	4	0	2	1034	972
8	10	1	250	251	4	-10	2	340	317	0	-6	2	747	718	5	-3	2	706	628	6	0	2	956	887
-5	11	1	444	428	6	-10	2	330	309	2	-6	2	1085	1024	7	-3	2	972	921	8	0	2	644	642
-3	11	1	427	418	8	-10	2	310	297	4	-6	2	528	473	9	-3	2	515	495	10	0	2	348	358
-1	11	1	360	403	-7	-9	2	348	363	6	-6	2	661	610	11	-3	2	394	407	12	0	2	408	434
1	11	1	586	531	-5	-9	2	462	468	8	-6	2	564	527	-10	-2	2	355	362	-11	1	2	231	248
3	11	1	307	277	-3	-9	2	790	771	10	-6	2	295	296	-8	-2	2	816	816	-9	1	2	538	538
5	11	1	300	307	-1	-9	2	539	530	-9	-5	2	546	567	-6	-2	2	446	439	-7	1	2	563	556
7	11	1	316	306	1	-9	2	559	615	-7	-5	2	562	559	-4	-2	2	983	949	-5	1	2	867	804
-4	12	1	380	370	3	-9	2	543	502	-5	-5	2	653	649	-2	-2	2	972	958	-3	1	2	1739	1718
-2	12	1	247	301	5	-9	2	436	395	-3	-5	2	1268	1207	0	-2	2	833	949	-1	1	2	366	397
0	12	1	473	453	7	-9	2	466	441	-1	-5	2	662	661	2	-2	2	1964	1897	1	1	2	1381	1435
2	12	1	461	414	9	-9	2	234	234	1	-5	2	1018	1167	4	-2	2	675	600	3	1	2	1838	1745
4	12	1	285	279	-8	-8	2	433	456	3	-5	2	1084	982	6	-2	2	985	897	5	1	2	1119	1036
-3	13	1	260	275	-6	-8	2	305	300	5	-5	2	512	474	8	-2	2	777	752	7	1	2	1071	1028
-1	13	1	265	276	-4	-8	2	688	665	7	-5	2	746	709	10	-2	2	377	373	9	1	2	435	428
1	13	1	386	367	-2	-8	2	765	739	9	-5	2	500	488	12	-2	2	389	407	11	1	2	415	433
3	13	1	281	251	0	-8	2	576	558	11	-5	2	329	347	-11	-1	2	254	274	-10	2	2	303	310
-1	-13	2	269	284	2	-8	2	669	669	-10	-4	2	305	328	-9	-1	2	637	637	-8	2	2	621	598
1	-13	2	349	330	4	-8	2	614	576	-8	-4	2	759	774	-7	-1	2	616	617	-6	2	2	442	426
-4	-12	2	378	372	6	-8	2	802	739	-6	-4	2	492	472	-5	-1	2	862	820	-4	2	2	1035	1015

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-2	2	2	914	944	1	5	2	1164	1163	-7	9	2	285	277	-3	-11	3	266	267	5	-7	3	647	604
0	2	2	767	893	3	5	2	1250	1145	-5	9	2	570	366	-1	-11	3	429	437	7	-7	3	420	390
2	2	2	1934	1893	5	5	2	875	824	-3	9	2	557	582	1	-11	3	346	380	9	-7	3	419	407
4	2	2	893	818	7	5	2	990	969	-1	9	2	306	360	3	-11	3	443	450	-8	-6	3	442	459
6	2	2	1165	1082	9	5	2	388	401	1	9	2	797	793	5	-11	3	323	315	-6	-6	3	587	590
8	2	2	783	774	11	5	2	284	310	3	9	2	989	919	-6	-10	3	314	331	-4	-6	3	660	641
10	2	2	308	317	-10	6	2	289	295	5	9	2	422	410	-4	-10	3	294	287	-2	-6	3	893	882
12	2	2	401	417	-8	6	2	560	551	7	9	2	465	459	-2	-10	3	541	536	0	-6	3	428	456
-11	3	2	239	253	-6	6	2	238	222	9	9	2	282	287	0	-10	3	401	403	2	-6	3	636	663
-9	3	2	515	519	-4	6	2	594	582	-6	10	2	265	268	2	-10	3	353	395	4	-6	3	728	685
-7	3	2	721	711	-2	6	2	979	1040	-4	10	2	438	457	4	-10	3	358	346	6	-6	3	383	359
-5	3	2	855	828	0	6	2	674	724	-2	10	2	366	439	6	-10	3	244	230	8	-6	3	592	568
-3	3	2	1397	1410	2	6	2	1082	1023	0	10	2	342	354	-7	-9	3	442	451	10	-6	3	312	315
-1	3	2	750	883	4	6	2	665	624	2	10	2	649	616	-5	-9	3	398	391	-9	-5	3	343	356
1	3	2	1393	1449	6	6	2	713	693	4	10	2	351	334	-3	-9	3	633	612	-7	-5	3	648	644
3	3	2	642	628	8	6	2	518	527	6	10	2	330	318	-1	-9	3	567	549	-5	-5	3	615	595
5	3	2	340	325	10	6	2	269	298	8	10	2	361	356	1	-9	3	321	344	-3	-5	3	935	906
7	3	2	1036	997	-9	7	2	429	436	-5	11	2	313	326	3	-9	3	634	618	-1	-5	3	839	855
9	3	2	430	426	-7	7	2	564	548	-3	11	2	402	453	5	-9	3	355	337	1	-5	3	642	718
11	3	2	323	346	-5	7	2	560	557	-1	11	2	284	310	7	-9	3	313	300	3	-5	3	1020	988
-10	4	2	347	360	-3	7	2	906	946	1	11	2	362	358	-8	-8	3	346	351	5	-5	3	555	516
-8	4	2	774	752	-1	7	2	471	551	3	11	2	346	327	-6	-8	3	367	365	7	-5	3	675	642
-6	4	2	603	595	1	7	2	673	659	5	11	2	251	238	-4	-8	3	496	464	9	-5	3	551	543
-4	4	2	1108	1072	3	7	2	695	640	7	11	2	381	375	-2	-8	3	752	742	11	-5	3	143	152
-2	4	2	1280	1362	5	7	2	336	332	-4	12	2	321	328	0	-8	3	379	393	-10	-4	3	254	274
0	4	2	831	950	7	7	2	550	539	-2	12	2	308	357	2	-8	3	598	761	-8	-4	3	516	515
2	4	2	1336	1298	9	7	2	332	348	0	12	2	324	333	4	-8	3	993	928	-6	-4	3	509	502
4	4	2	377	361	-8	8	2	435	440	2	12	2	443	426	6	-8	3	406	378	-4	-4	3	665	623
6	4	2	945	898	-6	8	2	466	449	4	12	2	306	295	8	-8	3	413	399	-2	-4	3	1246	1249
8	4	2	776	781	-4	8	2	709	723	-1	13	2	248	261	-9	-7	3	240	234	0	-4	3	905	1007
10	4	2	285	301	-2	8	2	510	581	1	13	2	321	322	-7	-7	3	404	414	2	-4	3	1174	1206
-9	5	2	542	545	0	8	2	410	430	-2	-12	3	379	373	-5	-7	3	380	377	4	-4	3	1090	1006
-7	5	2	481	467	2	8	2	1073	1010	0	-12	3	318	319	-3	-7	3	735	721	6	-4	3	657	604
-5	5	2	252	245	4	8	2	601	571	2	-12	3	309	359	-1	-7	3	632	636	8	-4	3	833	789
-3	5	2	1116	1102	6	8	2	472	459	4	-12	3	343	329	1	-7	3	429	471	10	-4	3	302	304
-1	5	2	849	1000	8	8	2	451	461	-5	-11	3	149	142	3	-7	3	1060	1030	-9	-3	3	422	434

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-7	-3	3	606	597	-6	0	3	879	849	-5	3	3	553	528	2	6	3	828	828	2	10	3	450	437
-5	-3	3	406	398	-4	0	3	855	794	-3	3	3	1048	1053	4	6	3	825	795	4	10	3	353	336
-3	-3	3	1101	1089	-2	0	3	1067	1104	-1	3	3	860	1004	6	6	3	452	444	6	10	3	311	308
-1	-3	3	1285	1373	0	0	3	927	1062	1	3	3	558	613	8	6	3	569	562	-5	11	3	200	202
1	-3	3	695	782	2	0	3	1542	1572	3	3	3	993	997	10	6	3	336	353	-3	11	3	303	346
3	-3	3	999	970	4	0	3	1225	1163	5	3	3	835	795	-9	7	3	338	328	-1	11	3	282	301
5	-3	3	789	719	6	0	3	497	472	7	3	3	624	623	-7	7	3	513	508	1	11	3	224	233
7	-3	3	793	747	8	0	3	740	736	9	3	3	524	530	-5	7	3	417	405	3	11	3	381	381
9	-3	3	665	642	10	0	3	456	467	11	3	3	263	279	-3	7	3	662	722	5	11	3	313	317
11	-3	3	263	269	12	0	3	276	291	-10	4	3	254	264	-1	7	3	490	549	-2	12	3	346	384
-10	-2	3	278	308	-11	1	3	204	212	-8	4	3	613	605	1	7	3	465	459	0	12	3	277	283
-8	-2	3	649	654	-9	1	3	389	391	-6	4	3	580	565	3	7	3	685	670	2	12	3	371	370
-6	-2	3	560	554	-7	1	3	771	780	-4	4	3	802	786	5	7	3	430	423	4	12	3	379	363
-4	-2	3	643	629	-5	1	3	652	644	-2	4	3	1119	1221	7	7	3	506	504	0	-12	4	302	300
-2	-2	3	1355	1411	-3	1	3	913	936	0	4	3	549	633	9	7	3	450	464	2	-12	4	235	252
0	-2	3	773	893	-1	1	3	841	974	2	4	3	845	862	-8	8	3	413	420	-3	-11	4	317	304
2	-2	3	580	607	1	1	3	939	1046	4	4	3	1092	1029	-6	8	3	419	409	-1	-11	4	446	450
4	-2	3	916	885	3	1	3	1645	1599	6	4	3	727	685	-4	8	3	377	382	1	-11	4	248	273
6	-2	3	703	648	5	1	3	786	716	8	4	3	635	627	-2	8	3	533	629	3	-11	4	345	380
8	-2	3	796	770	7	1	3	614	582	10	4	3	302	327	0	8	3	579	606	5	-11	4	374	364
10	-2	3	409	416	9	1	3	732	719	-9	5	3	299	309	2	8	3	768	752	-4	-10	4	242	247
12	-2	3	307	320	11	1	3	359	379	-7	5	3	410	405	4	8	3	523	506	-2	-10	4	468	456
-11	-1	3	265	270	-10	2	3	178	192	-5	5	3	451	446	6	8	3	414	402	0	-10	4	313	334
-9	-1	3	415	424	-8	2	3	644	642	-3	5	3	1092	1126	8	8	3	456	472	2	-10	4	216	240
-7	-1	3	777	774	-6	2	3	596	595	-1	5	3	741	840	-7	9	3	355	355	4	-10	4	371	385
-5	-1	3	658	623	-4	2	3	633	623	1	5	3	722	719	-5	9	3	253	263	6	-10	4	299	293
-3	-1	3	983	993	-2	2	3	1089	1173	3	5	3	1300	1227	-3	9	3	442	486	-5	-9	4	381	377
-1	-1	3	1123	1242	0	2	3	669	789	5	5	3	827	771	-1	9	3	586	543	-3	-9	4	397	381
1	-1	3	951	1090	2	2	3	1171	1205	7	5	3	594	585	1	9	3	730	723	-1	-9	4	503	499
3	-1	3	1332	1300	4	2	3	1292	1227	9	5	3	478	482	3	9	3	651	610	1	-9	4	323	347
5	-1	3	813	759	6	2	3	573	561	11	5	3	220	234	5	9	3	324	315	3	-9	4	420	440
7	-1	3	687	663	8	2	3	683	679	-8	6	3	365	370	7	9	3	403	399	5	-9	4	337	331
9	-1	3	613	604	10	2	3	457	468	-6	6	3	334	322	-8	10	3	281	276	7	-9	4	289	279
11	-1	3	264	274	12	2	3	283	306	-4	6	3	683	699	-4	10	3	273	294	-6	-8	4	446	449
-10	0	3	240	248	-9	3	3	416	420	-2	6	3	867	974	-2	10	3	415	476	-4	-8	4	365	345
-8	0	3	677	662	-7	3	3	797	777	0	6	3	412	451	0	10	3	358	371	-2	-8	4	571	558

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
0	-8	4	607	637	-4	-4	4	435	470	3	-1	4	1140	1125	8	2	4	702	689	-2	6	4	522	577
2	-8	4	646	726	-2	-4	4	1120	1132	5	-1	4	966	831	10	2	4	452	468	0	6	4	564	609
4	-8	4	617	609	0	-4	4	965	1035	7	-1	4	415	405	-9	3	4	283	287	2	6	4	550	556
6	-8	4	290	275	2	-4	4	721	757	9	-1	4	561	530	-7	3	4	609	589	4	6	4	797	788
8	-8	4	353	355	4	-4	4	1113	1072	11	-1	4	256	266	-5	3	4	561	550	6	6	4	412	400
-7	-7	4	410	418	6	-4	4	631	598	-10	0	4	253	256	-3	3	4	599	605	8	6	4	449	440
-5	-7	4	424	412	8	-4	4	452	436	-8	0	4	412	400	-1	3	4	1048	1145	10	6	4	346	361
-3	-7	4	417	393	10	-4	4	278	279	-6	0	4	774	771	1	3	4	566	599	-7	7	4	415	414
-1	-7	4	675	696	-9	-3	4	194	198	-4	0	4	419	412	3	3	4	988	974	-5	7	4	433	433
1	-7	4	574	628	-7	-3	4	543	520	-2	0	4	1203	1258	5	3	4	736	726	-3	7	4	365	378
3	-7	4	751	779	-5	-3	4	585	580	0	0	4	1185	1333	7	3	4	380	375	-1	7	4	611	658
5	-7	4	485	453	-3	-3	4	808	792	2	0	4	869	907	9	3	4	513	518	1	7	4	369	390
7	-7	4	364	345	-1	-3	4	1047	1100	4	0	4	1043	1020	11	3	4	250	266	3	7	4	616	612
9	-7	4	441	448	1	-3	4	274	301	6	0	4	502	479	-8	4	4	350	342	5	7	4	613	585
-8	-6	4	378	380	3	-3	4	1017	1033	8	0	4	686	666	-6	4	4	717	697	7	7	4	341	335
-6	-6	4	665	648	5	-3	4	973	935	10	0	4	428	443	-4	4	4	456	457	9	7	4	382	395
-4	-6	4	341	306	7	-3	4	474	530	-9	1	4	262	265	-2	4	4	813	891	-6	8	4	379	383
-2	-6	4	595	593	9	-3	4	556	550	-7	1	4	680	655	0	4	4	788	852	-4	8	4	262	280
0	-6	4	525	567	11	-3	4	321	335	-5	1	4	538	538	2	4	4	687	688	-2	8	4	603	642
2	-6	4	387	420	-10	-2	4	303	306	-3	1	4	518	517	4	4	4	1101	1058	0	8	4	587	609
4	-6	4	649	643	-8	-2	4	393	373	-1	1	4	1141	1287	6	4	4	480	468	2	8	4	349	351
6	-6	4	445	422	-6	-2	4	710	697	1	1	4	702	786	8	4	4	463	464	4	8	4	661	628
8	-6	4	467	460	-4	-2	4	547	525	3	1	4	956	949	10	4	4	382	395	6	8	4	387	381
10	-6	4	394	388	-2	-2	4	1031	1036	5	1	4	688	666	-9	5	4	139	143	8	8	4	316	319
-9	-5	4	246	241	0	-2	4	344	377	7	1	4	658	654	-7	5	4	515	506	-5	9	4	291	298
-7	-5	4	668	648	2	-2	4	317	343	9	1	4	775	780	-5	5	4	644	631	-3	9	4	376	417
-5	-5	4	552	515	4	-2	4	1276	1246	11	1	4	274	295	-3	5	4	454	482	-1	9	4	661	705
-3	-5	4	495	481	6	-2	4	600	568	-10	2	4	310	299	-1	5	4	775	856	1	9	4	344	340
-1	-5	4	945	980	8	-2	4	593	568	-8	2	4	413	405	1	5	4	589	616	3	9	4	398	390
1	-5	4	491	530	10	-2	4	490	493	-6	2	4	697	683	3	5	4	931	906	5	9	4	476	460
3	-5	4	698	712	-9	-1	4	259	259	-4	2	4	383	369	5	5	4	717	709	7	9	4	277	281
5	-5	4	723	696	-7	-1	4	668	648	-2	2	4	987	952	7	5	4	398	396	-4	10	4	228	234
7	-5	4	457	444	-5	-1	4	597	581	0	2	4	856	954	9	5	4	469	488	-2	10	4	377	416
9	-5	4	348	351	-3	-1	4	799	787	2	2	4	693	700	-8	6	4	240	235	0	10	4	347	359
-8	-4	4	295	298	-1	-1	4	1233	1348	4	2	4	997	975	-6	6	4	636	624	2	10	4	245	239
-6	-4	4	671	650	1	-1	4	532	599	6	2	4	449	442	-4	6	4	433	437	4	10	4	465	443

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 18-CROWN-6.HGCL2

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
6	10	4	315	310	3	-7	5	321	332	1	-3	5	778	851	-9	1	5	243	248	2	4	5	548	561
-3	11	4	203	225	5	-7	5	538	536	3	-3	5	723	749	-7	1	5	381	364	4	4	5	680	675
-1	11	4	295	326	7	-7	5	386	383	5	-3	5	784	787	-5	1	5	570	549	6	4	5	549	542
1	11	4	230	242	9	-7	5	341	327	7	-3	5	464	447	-3	1	5	430	438	8	4	5	326	334
3	11	4	379	378	-6	-6	5	373	366	9	-3	5	438	446	-1	1	5	854	911	10	4	5	413	426
5	11	4	333	330	-4	-6	5	330	327	-8	-2	5	225	230	1	1	5	669	721	-7	5	5	360	367
0	12	4	293	306	-2	-6	5	386	384	-6	-2	5	599	587	3	1	5	448	456	-5	5	5	450	451
2	12	4	297	281	0	-6	5	567	633	-4	-2	5	553	546	5	1	5	1012	1018	-3	5	5	287	298
-1	-11	5	306	294	2	-6	5	310	347	-2	-2	5	240	221	7	1	5	756	749	-1	5	5	636	676
1	-11	5	298	312	4	-6	5	521	533	0	-2	5	599	656	9	1	5	388	391	1	5	5	645	689
3	-11	5	247	280	6	-6	5	542	543	2	-2	5	715	781	11	1	5	321	333	3	5	5	562	572
-4	-10	5	284	288	8	-6	5	330	327	4	-2	5	764	760	-8	2	5	227	224	5	5	5	674	666
-2	-10	5	238	233	-7	-5	5	338	333	6	-2	5	625	616	-6	2	5	500	489	7	5	5	407	413
0	-10	5	315	345	-5	-5	5	479	477	8	-2	5	416	413	-4	2	5	463	472	9	5	5	382	393
2	-10	5	218	244	-3	-5	5	443	448	10	-2	5	465	478	-2	2	5	562	600	-6	6	5	457	462
4	-10	5	329	366	-1	-5	5	665	712	-9	-1	5	243	248	0	2	5	818	871	-4	6	5	304	305
-5	-9	5	376	370	1	-5	5	528	575	-7	-1	5	406	402	2	2	5	415	443	-2	6	5	363	379
-3	-9	5	248	241	3	-5	5	421	444	-5	-1	5	768	756	4	2	5	661	662	0	6	5	649	704
-1	-9	5	389	405	5	-5	5	677	671	-3	-1	5	546	566	6	2	5	738	792	2	6	5	484	496
1	-9	5	340	375	7	-5	5	266	261	-1	-1	5	739	792	8	2	5	382	387	4	6	5	514	506
3	-9	5	207	228	9	-5	5	299	303	1	-1	5	805	882	10	2	5	357	361	6	6	5	436	427
5	-9	5	408	428	-8	-4	5	232	232	3	-1	5	574	590	-9	3	5	243	243	8	6	5	303	312
7	-9	5	254	248	-6	-4	5	524	526	5	-1	5	648	646	-7	3	5	354	342	-7	7	5	297	287
-6	-8	5	375	372	-4	-4	5	643	636	7	-1	5	368	358	-5	3	5	617	615	-5	7	5	408	421
-4	-8	5	356	353	-2	-4	5	652	676	9	-1	5	347	349	-3	3	5	533	565	-3	7	5	277	298.
-2	-8	5	413	408	0	-4	5	862	925	11	-1	5	308	330	-1	3	5	792	852	-1	7	5	510	538
0	-8	5	684	725	2	-4	5	583	648	-8	0	5	266	261	1	3	5	628	681	1	7	5	503	522
2	-8	5	330	364	4	-4	5	683	693	-6	0	5	625	611	3	3	5	481	485	3	7	5	448	421
4	-8	5	337	353	6	-4	5	537	521	-4	0	5	663	672	5	3	5	626	633	5	7	5	457	432
6	-8	5	424	421	8	-4	5	205	201	-2	0	5	753	799	7	3	5	364	354	7	7	5	289	286
8	-8	5	245	233	10	-4	5	385	394	0	0	5	1061	1130	9	3	5	320	329	9	7	5	282	291
-7	-7	5	267	258	-9	-3	5	199	200	2	0	5	493	541	-9	4	5	238	243	-6	8	5	336	326
-5	-7	5	403	404	-7	-3	5	361	352	4	0	5	630	636	-6	4	5	503	509	-4	8	5	341	358
-3	-7	5	314	309	-5	-3	5	710	694	6	0	5	764	765	-4	4	5	475	496	-2	8	5	378	395
-1	-7	5	633	654	-3	-3	5	429	420	8	0	5	363	358	-2	4	5	560	605	0	8	5	456	473
1	-7	5	607	641	-1	-3	5	526	554	10	0	5	355	358	0	4	5	768	840	2	8	5	384	379

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 18-CROWN-6.HgCl2

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
4	8	5	487	481	5	-7	6	424	446	-8	-2	6	246	243	7	1	6	446	430	7	5	6	452	451
6	8	5	353	362	7	-7	6	357	352	-6	-2	6	329	322	9	1	6	240	255	9	5	6	269	269
8	8	5	249	244	-6	-6	6	221	212	-4	-2	6	386	383	-8	2	6	183	186	-6	6	6	208	200
-5	9	5	338	345	-4	-6	6	440	438	-2	-2	6	204	203	-6	2	6	275	276	-4	6	6	374	378
-3	9	5	292	315	-2	-6	6	278	272	0	-2	6	825	867	-4	2	6	573	585	-2	6	6	321	321
-1	9	5	375	386	0	-6	6	453	470	2	-2	6	592	626	-2	2	6	315	325	0	6	6	566	560
1	9	5	311	316	2	-6	6	408	425	4	-2	6	371	387	0	2	6	543	572	2	6	6	392	398
3	9	5	363	367	4	-6	6	369	392	6	-2	6	634	633	2	2	6	534	572	4	6	6	261	248
5	9	5	438	432	6	-6	6	465	471	8	-2	6	382	386	4	2	6	561	573	6	6	6	481	466
7	9	5	254	255	8	-6	6	317	313	10	-2	6	322	312	6	2	6	607	600	8	6	6	269	277
-4	10	5	241	251	-7	-5	6	145	148	-7	-1	6	264	269	8	2	6	229	236	-5	7	6	324	336
-2	10	5	234	252	-5	-5	6	466	474	-5	-1	6	571	568	10	2	6	333	336	-3	7	6	320	328
0	10	5	322	327	-3	-5	6	434	429	-3	-1	6	429	428	-7	3	6	221	216	-1	7	6	362	355
2	10	5	263	267	-1	-5	6	366	362	-1	-1	6	529	540	-5	3	6	593	599	1	7	6	475	478
4	10	5	361	357	1	-5	6	547	563	1	-1	6	741	793	-3	3	6	508	517	3	7	6	196	184
-1	11	5	264	288	3	-5	6	340	368	3	-1	6	281	290	-1	3	6	363	370	5	7	6	342	333
1	11	5	299	298	5	-5	6	414	421	5	-1	6	496	486	1	3	6	609	640	7	7	6	338	347
3	11	5	249	250	7	-5	6	352	348	7	-1	6	402	400	3	3	6	325	336	-4	8	6	349	343
0	-10	6	298	296	9	-5	6	284	290	9	-1	6	286	290	5	3	6	447	439	-2	8	6	223	223
2	-10	6	293	310	-6	-4	6	378	363	-8	0	6	286	279	7	3	6	362	357	0	8	6	419	418
-3	-9	6	259	246	-4	-4	6	621	617	-6	0	6	399	383	9	3	6	294	296	2	8	6	396	394
-1	-9	6	250	256	-2	-4	6	386	384	-4	0	6	680	695	-6	4	6	306	313	4	8	6	299	282
1	-9	6	316	332	0	-4	6	659	694	-2	0	6	468	466	-4	4	6	584	593	6	8	6	379	377
3	-9	6	250	278	2	-4	6	500	534	0	0	6	673	707	-2	4	6	335	329	-3	9	6	232	231
5	-9	6	301	309	4	-4	6	364	373	2	0	6	489	522	0	4	6	590	607	-1	9	6	226	223
-4	-8	6	371	368	6	-4	6	435	435	4	0	6	522	535	2	4	6	550	578	1	9	6	410	417
-2	-8	6	323	322	8	-4	6	304	300	6	0	6	618	598	4	4	6	402	392	3	9	6	299	301
0	-8	6	402	417	-7	-3	6	215	235	8	0	6	249	244	6	4	6	535	523	5	9	6	342	314
2	-8	6	293	304	-5	-3	6	503	488	10	0	6	335	333	8	4	6	337	340	0	10	6	285	281
4	-8	6	312	328	-3	-3	6	319	307	-7	1	6	165	166	-7	5	6	146	142	2	10	6	284	280
6	-8	6	359	361	-1	-3	6	504	530	-5	1	6	477	471	-5	5	6	345	345	-2	-8	7	265	260
-5	-7	6	354	358	1	-3	6	840	884	-3	1	6	486	494	-3	5	6	370	375	0	-8	7	228	220
-3	-7	6	376	370	3	-3	6	386	400	-1	1	6	449	454	-1	5	6	419	424	2	-8	7	370	383
-1	-7	6	390	405	5	-3	6	575	568	1	1	6	656	701	1	5	6	690	700	4	-8	7	242	248
1	-7	6	460	467	7	-3	6	501	492	3	1	6	593	617	3	5	6	406	412	-3	-7	7	364	354
3	-7	6	284	307	9	-3	6	326	324	5	1	6	893	887	5	5	6	524	518	-1	-7	7	227	226

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 18-CROWN-6.HGCL2 PAGE 9

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
1	-7	7	332	337	6	-2	7	443	447	-1	3	7	261	258	4	-6	8	255	252	3	1	8	379	383
3	-7	7	335	356	8	-2	7	363	361	1	3	7	466	457	-1	-5	8	269	250	5	1	8	206	203
5	-7	7	245	258	-5	-1	7	271	270	3	3	7	346	357	1	-5	8	314	298	7	1	8	360	344
-4	-6	7	332	321	-3	-1	7	505	492	5	3	7	281	257	3	-5	8	345	339	-4	2	8	211	192
-2	-6	7	294	286	-1	-1	7	373	362	7	3	7	407	414	5	-5	8	223	214	-2	2	8	397	374
0	-6	7	266	265	1	-1	7	426	417	-4	4	7	357	361	-2	-4	8	334	328	0	2	8	295	274
2	-6	7	422	437	3	-1	7	392	406	-2	4	7	326	316	0	-4	8	253	242	2	2	8	399	390
4	-6	7	256	284	5	-1	7	281	299	0	4	7	428	411	2	-4	8	402	394	4	2	8	267	263
6	-6	7	320	334	7	-1	7	435	443	2	4	7	497	496	4	-4	8	273	275	6	2	8	276	270
-5	-5	7	291	276	9	-1	7	256	260	4	4	7	317	310	6	-4	8	244	240	-3	3	8	313	296
-3	-5	7	366	367	-6	0	7	248	235	6	4	7	404	390	-3	-3	8	402	381	-1	3	8	306	293
-1	-5	7	254	239	-4	0	7	479	480	8	4	7	317	310	-1	-3	8	269	243	1	3	8	257	240
1	-5	7	420	422	-2	0	7	412	404	-5	5	7	244	238	1	-3	8	287	284	3	3	8	350	346
3	-5	7	385	404	0	0	7	363	350	-3	5	7	391	391	3	-3	8	401	404	5	3	8	244	247
5	-5	7	263	265	2	0	7	611	614	-1	5	7	360	344	5	-3	8	240	247	-2	4	8	408	379
7	-5	7	378	381	4	0	7	370	363	1	5	7	467	465	-4	-2	8	305	285	0	4	8	253	238
-4	-4	7	391	398	6	0	7	329	319	3	5	7	408	407	-2	-2	8	403	386	2	4	8	358	338
-2	-4	7	397	393	8	0	7	374	381	5	5	7	361	351	0	-2	8	183	171	4	4	8	305	304
0	-4	7	349	333	-5	1	7	309	310	7	5	7	359	349	2	-2	8	397	394	6	4	8	246	225
2	-4	7	493	506	-3	1	7	462	464	-4	6	7	344	334	4	-2	8	354	352	-1	5	8	297	277
4	-4	7	290	302	-1	1	7	318	308	-2	6	7	338	325	6	-2	8	286	280	1	5	8	253	254
6	-4	7	343	347	1	1	7	640	627	0	6	7	252	251	-3	-1	8	396	383	3	5	8	394	378
8	-4	7	336	329	3	1	7	650	669	2	6	7	304	307	-1	-1	8	267	258	5	5	8	214	206
-5	-3	7	220	222	5	1	7	315	301	4	6	7	296	300	1	-1	8	287	266	0	6	8	138	121
-3	-3	7	473	484	7	1	7	361	367	6	6	7	350	338	3	-1	8	399	405	2	6	8	352	321
-1	-3	7	410	416	9	1	7	294	290	-3	7	7	341	321	5	-1	8	279	278	4	6	8	293	287
1	-3	7	462	453	-6	2	7	227	211	-1	7	7	221	210	7	-1	8	319	310	0	-2	9	249	223
3	-3	7	433	451	-4	2	7	404	389	1	7	7	240	233	-4	0	8	270	249	2	-2	9	248	227
5	-3	7	349	351	-2	2	7	321	310	3	7	7	263	266	-2	0	8	394	387	1	-1	9	217	201
7	-3	7	423	428	0	2	7	387	375	5	7	7	300	295	0	0	8	299	284	3	-1	9	313	295
-6	-2	7	128	128	2	2	7	622	627	-2	8	7	266	252	2	0	8	429	419	0	0	9	298	248
-4	-2	7	340	334	4	2	7	351	352	0	8	7	282	272	4	0	8	278	275	2	0	9	216	199
-2	-2	7	503	501	6	2	7	312	310	2	8	7	338	334	6	0	8	280	290	4	0	9	340	316
0	-2	7	410	401	8	2	7	366	371	4	8	7	270	259	-3	1	8	357	344	1	1	9	218	185
2	-2	7	468	471	-5	3	7	337	336	0	-6	8	196	184	-1	1	8	368	342	3	1	9	272	244
4	-2	7	354	369	-3	3	7	358	346	2	-6	8	317	307	1	1	8	410	395	0	2	9	253	226

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 18-CROWN-6.HGCL2 PAGE 10

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
2	2	9	205	187																				

DEVIATIONS GREATER THAN 2 SIGMA

H	K	L	FO	FC	D/SIGMA
-1	1	0	179.33	202.75	2.30
-3	3	0	121.67	107.53	2.04
-1	7	0	89.27	102.97	2.70
-2	12	0	25.35	28.55	2.14
1	-7	1	109.49	124.73	2.45
2	-6	1	131.13	114.79	2.15
2	-2	1	166.55	146.20	2.15
3	-1	1	104.87	91.32	2.27
-2	0	1	228.28	262.15	2.61
0	0	1	127.53	201.89	10.25
-1	5	1	72.63	81.72	2.20
-1	7	1	67.89	77.18	2.40
3	7	1	52.81	46.58	2.07
-1	9	1	41.17	46.71	2.36
-1	11	1	35.96	40.33	2.11
-2	12	1	24.74	30.06	3.64
2	-12	2	38.69	44.34	2.55
1	-7	2	72.01	82.18	2.48
1	-5	2	101.83	116.73	2.57
0	-2	2	83.26	94.94	2.47
-1	-1	2	26.86	31.03	2.72
0	0	2	24.01	30.07	4.42
0	2	2	76.73	89.27	2.87
-1	3	2	74.98	88.28	3.12
0	4	2	83.12	95.04	2.52
-1	5	2	84.93	100.04	3.13
-1	7	2	47.12	55.07	2.96
-2	8	2	50.98	58.10	2.45
-1	9	2	30.61	35.97	3.06
-2	10	2	36.63	43.87	3.45
-3	11	2	40.16	45.33	2.25
-2	12	2	30.77	35.72	2.79
2	-12	3	30.85	35.90	2.84
2	-10	3	35.34	39.45	2.03
1	-5	3	64.22	71.81	2.08
1	-3	3	69.54	78.23	2.20
0	-2	3	77.33	89.28	2.72
1	-1	3	95.12	109.02	2.57
0	0	3	92.73	106.15	2.54
-1	1	3	84.14	97.40	2.77
0	2	3	66.91	73.91	3.15
-1	3	3	85.96	100.39	2.95
0	4	3	54.90	63.31	2.69
-1	5	3	74.08	83.97	2.35
-2	6	3	86.70	97.33	2.17
-1	7	3	49.03	54.86	2.09
-2	8	3	53.34	62.91	3.15
-2	10	3	41.55	47.62	2.56
-3	11	3	30.34	34.60	2.44
2	-8	4	64.58	72.64	2.19

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Appendix II. Structure factor table for $CdCl_2 \cdot 18\text{-Crown-}6$

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR 18-CROWN-6.CDCL2 PAGE 1

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
2	0	0	679	772	-1	3	0	865	1015	2	6	0	310	297	-4	10	0	244	241	1	-11	1	200	186
4	0	0	541	561	1	3	0	754	854	4	6	0	455	439	-2	10	0	96	93	3	-11	1	112	114
6	0	0	615	635	3	3	0	579	570	6	6	0	381	382	0	10	0	400	399	5	-11	1	188	179
8	0	0	204	202	5	3	0	872	999	8	6	0	143	148	2	10	0	100	95	7	-11	1	150	152
10	0	0	313	299	7	3	0	134	-144	10	6	0	296	297	4	10	0	163	159	-6	-10	1	50	52
12	0	0	33	34	9	3	0	132	127	-9	7	0	241	240	6	10	0	243	246	-4	-10	1	307	307
-11	1	0	170	163	11	3	0	216	218	-7	7	0	69	70	8	10	0	63	62	-2	-10	1	171	169
-9	1	0	316	304	-10	4	0	216	208	-5	7	0	506	506	-7	11	0	77	72	0	-10	1	251	250
-7	1	0	214	205	-8	4	0	109	118	-3	7	0	413	398	-5	11	0	244	239	2	-10	1	305	319
-5	1	0	761	782	-6	4	0	592	596	-1	7	0	552	572	-3	11	0	83	71	4	-10	1	124	130
-3	1	0	83	-67	-4	4	0	869	995	1	7	0	571	569	-1	11	0	178	163	6	-10	1	235	227
-1	1	0	1164	1426	-2	4	0	562	568	3	7	0	100	97	1	11	0	286	277	8	-10	1	36	41
1	1	0	1196	1418	0	4	0	1243	1400	5	7	0	429	430	3	11	0	90	96	-7	-9	1	136	136
3	1	0	298	-266	2	4	0	532	516	7	7	0	73	74	5	11	0	210	211	-5	-9	1	221	224
5	1	0	804	929	4	4	0	901	1016	9	7	0	155	149	7	11	0	38	40	-3	-9	1	349	349
7	1	0	414	408	6	4	0	453	455	-8	8	0	113	102	-4	12	0	129	130	-1	-9	1	293	302
9	1	0	471	477	8	4	0	71	-72	-6	8	0	185	181	-2	12	0	61	63	1	-9	1	511	526
11	1	0	280	280	10	4	0	344	340	-4	8	0	403	402	0	12	0	273	278	3	-9	1	96	114
-12	2	0	89	83	-11	5	0	148	141	-2	8	0	421	411	2	12	0	156	159	5	-9	1	192	184
-10	2	0	451	433	-9	5	0	170	161	0	8	0	743	732	4	12	0	170	171	7	-9	1	240	230
-8	2	0	262	264	-7	5	0	165	165	2	8	0	122	112	-3	13	0	69	62	9	-9	1	59	58
-6	2	0	492	509	-5	5	0	845	839	4	8	0	312	315	-1	13	0	174	182	-8	-8	1	249	251
-4	2	0	538	561	-3	5	0	194	216	6	8	0	394	412	1	13	0	193	192	-6	-8	1	127	131
-2	2	0	352	-359	-1	5	0	126	132	8	8	0	118	107	3	13	0	62	57	-4	-8	1	385	386
0	2	0	570	626	1	5	0	737	746	-9	9	0	157	144	-3	-13	1	182	186	-2	-8	1	254	243
2	2	0	371	-360	3	5	0	413	413	-7	9	0	67	64	-1	-13	1	138	141	0	-8	1	583	574
4	2	0	756	767	5	5	0	874	852	-5	9	0	267	285	1	-13	1	222	222	2	-8	1	450	446
6	2	0	608	604	7	5	0	209	219	-3	9	0	146	155	3	-13	1	85	81	4	-8	1	27	-21
8	2	0	191	180	9	5	0	367	364	-1	9	0	407	417	-4	-12	1	262	268	6	-8	1	401	394
10	2	0	466	460	11	5	0	268	263	1	9	0	380	373	-2	-12	1	110	114	8	-8	1	223	223
12	2	0	104	106	-10	6	0	266	265	3	9	0	28	26	0	-12	1	127	124	-9	-7	1	255	252
-11	3	0	207	199	-8	6	0	81	81	5	9	0	449	464	2	-12	1	145	150	-7	-7	1	83	82
-9	3	0	343	360	-6	6	0	370	374	7	9	0	234	237	4	-12	1	77	75	-5	-7	1	294	288
-7	3	0	232	249	-4	6	0	537	540	9	9	0	161	156	-5	-11	1	177	182	-3	-7	1	391	384
-5	3	0	855	892	-2	6	0	184	-171	-8	10	0	63	55	-3	-11	1	226	227	-1	-7	1	257	251
-3	3	0	555	552	0	6	0	516	534	-6	10	0	196	202	-1	-11	1	39	-22	1	-7	1	811	820

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
3	-7	1	204	202	8	-4	1	74	73	9	-1	1	59	60	10	2	1	257	250	11	5	1	246	243
5	-7	1	219	221	10	-4	1	184	174	11	-1	1	243	234	12	2	1	172	169	-10	6	1	187	184
7	-7	1	378	396	-11	-3	1	36	35	-10	0	1	325	321	-11	3	1	155	161	-8	6	1	236	222
9	-7	1	128	131	-9	-3	1	212	205	-8	0	1	372	374	-9	3	1	406	424	-6	6	1	203	215
-10	-6	1	233	237	-7	-3	1	295	294	-6	0	1	186	196	-7	3	1	176	159	-4	6	1	289	302
-8	-6	1	244	234	-5	-3	1	816	825	-4	0	1	1161	1306	-5	3	1	787	807	-2	6	1	135	-131
-6	-6	1	172	168	-3	-3	1	563	567	-2	0	1	1803	2086	-3	3	1	740	767	0	6	1	826	818
-4	-6	1	623	620	-1	-3	1	390	363	0	0	1	1405	1435	-1	3	1	356	354	2	6	1	569	556
-2	-6	1	192	198	1	-3	1	1281	1420	2	0	1	368	372	1	3	1	1299	1429	4	6	1	165	153
0	-6	1	373	386	3	-3	1	499	509	4	0	1	371	390	3	3	1	579	573	6	6	1	522	525
2	-6	1	700	707	5	-3	1	559	607	6	0	1	852	874	5	3	1	25	31	8	6	1	185	187
4	-6	1	157	160	7	-3	1	497	504	8	0	1	158	153	7	3	1	204	197	10	6	1	147	140
6	-6	1	415	421	9	-3	1	104	105	10	0	1	147	149	9	3	1	135	136	-9	7	1	247	237
8	-6	1	122	126	11	-3	1	295	286	12	0	1	189	183	11	3	1	233	222	-7	7	1	140	139
10	-6	1	172	166	-10	-2	1	303	293	-11	1	1	125	120	-10	4	1	242	243	-5	7	1	545	551
-11	-5	1	139	142	-8	-2	1	351	338	-9	1	1	420	422	-8	4	1	353	362	-3	7	1	501	494
-9	-5	1	354	352	-6	-2	1	326	333	-7	1	1	83	85	-6	4	1	473	463	-1	7	1	342	335
-7	-5	1	251	255	-4	-2	1	668	677	-5	1	1	498	494	-4	4	1	847	995	1	7	1	571	581
-5	-5	1	623	614	-2	-2	1	91	-75	-3	1	1	888	1001	-2	4	1	430	416	3	7	1	51	48
-3	-5	1	595	618	0	-2	1	384	371	-1	1	1	697	782	0	4	1	1068	1189	5	7	1	229	226
-1	-5	1	96	105	2	-2	1	721	852	1	1	1	597	625	2	4	1	984	1094	7	7	1	186	186
1	-5	1	735	827	4	-2	1	290	300	3	1	1	356	357	4	4	1	203	220	9	7	1	13	10
3	-5	1	509	509	6	-2	1	742	762	5	1	1	853	975	6	4	1	297	307	-8	8	1	149	144
5	-5	1	439	437	8	-2	1	263	261	7	1	1	792	780	8	4	1	208	211	-6	8	1	182	185
7	-5	1	277	273	10	-2	1	238	228	9	1	1	190	202	10	4	1	268	258	-4	8	1	656	661
9	-5	1	48	38	12	-2	1	200	197	11	1	1	284	277	-11	5	1	41	38	-2	8	1	336	326
11	-5	1	279	268	-11	-1	1	190	188	-10	2	1	385	380	-9	5	1	335	330	0	8	1	345	348
-10	-4	1	152	152	-9	-1	1	512	525	-8	2	1	256	253	-7	5	1	242	248	2	8	1	297	303
-8	-4	1	269	276	-7	-1	1	188	188	-6	2	1	102	101	-5	5	1	440	453	4	8	1	320	327
-6	-4	1	495	479	-5	-1	1	493	495	-4	2	1	646	671	-3	5	1	32	38	6	8	1	413	413
-4	-4	1	796	916	-3	-1	1	913	993	-2	2	1	289	-264	-1	5	1	360	365	8	8	1	70	64
-2	-4	1	312	301	-1	-1	1	733	781	0	2	1	379	364	1	5	1	1076	1203	-7	9	1	23	17
0	-4	1	818	907	1	-1	1	577	632	2	2	1	887	1015	3	5	1	528	510	-5	9	1	236	250
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H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
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5	9	1	511	516	-1	-11	2	67	-70	1	-7	2	453	441	8	-4	2	332	334	9	-1	2	90	91
7	9	1	247	244	1	-11	2	252	250	3	-7	2	240	246	10	-4	2	202	200	11	-1	2	186	176
9	9	1	63	62	3	-11	2	223	227	5	-7	2	306	319	-11	-3	2	14	-14	-10	0	2	133	133
-6	10	1	73	84	5	-11	2	92	89	7	-7	2	439	440	-9	-3	2	372	362	-8	0	2	477	479
-4	10	1	305	299	7	-11	2	192	193	9	-7	2	50	42	-7	-3	2	490	490	-6	0	2	343	331
-2	10	1	107	101	-6	-10	2	76	79	-10	-6	2	83	81	-5	-3	2	110	103	-4	0	2	1314	1481
0	10	1	245	251	-4	-10	2	296	292	-8	-6	2	350	350	-3	-3	2	803	795	-2	0	2	971	1011
2	10	1	175	175	-2	-10	2	216	221	-6	-6	2	116	117	-1	-3	2	408	389	0	0	2	443	-363
4	10	1	167	160	0	-10	2	168	168	-4	-6	2	533	524	1	-3	2	1099	1195	2	0	2	1345	1427
6	10	1	252	250	2	-10	2	370	390	-2	-6	2	517	512	3	-3	2	706	743	4	0	2	420	409
8	10	1	42	44	4	-10	2	41	40	0	-6	2	327	314	5	-3	2	179	197	6	0	2	523	527
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-3	11	1	212	196	8	-10	2	93	102	4	-6	2	62	58	9	-3	2	179	180	10	0	2	91	82
-1	11	1	123	129	-7	-9	2	184	183	6	-6	2	299	305	11	-3	2	236	231	12	0	2	244	233
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5	11	1	111	102	-1	-9	2	247	259	-9	-5	2	320	332	-6	-2	2	81	83	-7	1	2	341	342
7	11	1	99	105	1	-9	2	322	328	-7	-5	2	375	380	-4	-2	2	522	500	-5	1	2	380	373
-4	12	1	216	214	3	-9	2	194	193	-5	-5	2	246	255	-2	-2	2	594	562	-3	1	2	1194	1324
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2	12	1	209	207	9	-9	2	38	43	1	-5	2	774	753	4	-2	2	89	100	3	1	2	1087	1192
4	12	1	71	66	-8	-8	2	277	284	3	-5	2	549	562	6	-2	2	486	500	5	1	2	636	635
-3	13	1	134	131	-6	-8	2	44	44	5	-5	2	99	95	8	-2	2	372	371	7	1	2	669	667
-1	13	1	100	100	-4	-8	2	354	356	7	-5	2	367	367	10	-2	2	121	119	9	1	2	76	75
1	13	1	211	203	-2	-8	2	453	455	9	-5	2	183	180	12	-2	2	216	211	11	1	2	243	231
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10	2	2	61	55	-10	6	2	77	75	5	9	2	143	139	-2	-10	3	327	321	2	-6	3	252	253
12	2	2	251	244	-8	6	2	344	345	7	9	2	241	242	0	-10	3	139	147	4	-6	3	291	298
-11	3	2	90	96	-6	6	2	75	-76	9	9	2	76	83	2	-10	3	141	134	6	-6	3	30	28
-9	3	2	275	260	-4	6	2	202	201	-6	10	2	81	75	4	-10	3	98	97	8	-6	3	294	289
-7	3	2	481	478	-2	6	2	726	732	-4	10	2	210	211	-7	-9	3	294	303	10	-6	3	63	80
-5	3	2	321	334	0	6	2	314	308	-2	10	2	207	207	-5	-9	3	215	216	-9	-5	3	162	165
-3	3	2	801	933	2	6	2	652	647	0	10	2	67	67	-3	-9	3	372	385	-7	-5	3	430	443
-1	3	2	390	385	4	6	2	214	214	2	10	2	405	407	-1	-9	3	296	300	-5	-5	3	282	281
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3	3	2	113	116	8	6	2	238	250	6	10	2	107	109	3	-9	3	362	355	-1	-5	3	561	539
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7	3	2	613	596	-9	7	2	228	226	-5	11	2	110	111	7	-9	3	104	109	3	-5	3	568	581
9	3	2	82	79	-7	7	2	360	354	-3	11	2	238	244	-8	-8	3	158	162	5	-5	3	115	117
11	3	2	167	161	-5	7	2	206	206	-1	11	2	64	69	-6	-8	3	195	192	7	-5	3	333	347
-10	4	2	156	153	-3	7	2	604	609	1	11	2	112	118	-4	-8	3	193	195	9	-5	3	262	280
-8	4	2	545	556	-1	7	2	146	147	3	11	2	100	94	-2	-8	3	477	477	11	-5	3	35	-31
-6	4	2	287	295	1	7	2	255	241	7	11	2	199	203	0	-8	3	56	56	-10	-4	3	129	133
-4	4	2	596	622	3	7	2	250	241	-4	12	2	147	158	2	-8	3	436	430	-8	-4	3	283	275
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2	4	2	755	837	9	7	2	74	81	2	12	2	227	228	8	-8	3	200	199	-2	-4	3	830	906
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8	4	2	427	426	-4	8	2	419	437	1	13	2	153	154	-5	-7	3	110	108	4	-4	3	559	560
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-9	5	2	315	319	0	8	2	30	30	0	-12	3	136	138	-1	-7	3	343	332	8	-4	3	511	521
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-5	5	2	131	-136	4	8	2	222	215	4	-12	3	162	169	3	-7	3	675	679	-9	-3	3	185	181
-3	5	2	761	794	6	8	2	195	189	-5	-11	3	40	-39	5	-7	3	294	295	-7	-3	3	377	373
-1	5	2	648	632	8	8	2	198	204	-3	-11	3	47	44	7	-7	3	150	141	-5	-3	3	90	85
1	5	2	778	757	-7	9	2	144	138	-1	-11	3	221	229	9	-7	3	171	163	-3	-3	3	667	657
3	5	2	720	724	-5	9	2	140	133	1	-11	3	143	149	-8	-6	3	253	255	-1	-3	3	954	998
5	5	2	430	423	-3	9	2	352	360	3	-11	3	247	243	-6	-6	3	365	375	1	-3	3	391	376
7	5	2	675	670	-1	9	2	61	59	5	-11	3	101	103	-4	-6	3	287	290	3	-3	3	520	530
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9	-3	3	349	353	-9	1	3	137	137	-4	4	3	420	424	5	7	3	101	106	4	12	3	180	186
11	-3	3	63	60	-7	1	3	570	572	-2	4	3	876	905	7	7	3	250	242	0	-12	4	160	167
-10	-2	3	115	116	-5	1	3	352	334	0	4	3	216	210	9	7	3	221	221	2	-12	4	88	92
-8	-2	3	358	374	-3	1	3	532	508	2	4	3	392	390	-8	8	3	262	264	-3	-11	4	114	118
-6	-2	3	355	348	-1	1	3	631	581	4	4	3	577	572	-6	8	3	271	267	-1	-11	4	283	295
-4	-2	3	199	197	1	1	3	595	535	6	4	3	345	327	-4	8	3	87	90	1	-11	4	74	70
-2	-2	3	903	953	3	1	3	1126	1218	8	4	3	358	356	-2	8	3	350	355	3	-11	4	189	187
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6	-2	3	243	246	11	1	3	169	170	-5	5	3	192	190	6	8	3	130	128	0	-10	4	118	120
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-5	-1	3	364	336	-2	2	3	803	804	5	5	3	438	421	-1	9	3	426	430	-1	-9	4	275	272
-3	-1	3	527	507	0	2	3	338	313	7	5	3	329	332	1	9	3	479	493	1	-9	4	107	98
-1	-1	3	790	776	2	2	3	709	761	9	5	3	211	215	3	9	3	378	371	3	-9	4	231	234
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3	-1	3	740	831	6	2	3	148	154	-8	6	3	148	152	7	9	3	196	194	7	-9	4	73	73
5	-1	3	319	317	8	2	3	343	348	-6	6	3	133	124	-6	10	3	145	137	-6	-8	4	314	321
7	-1	3	324	327	10	2	3	198	199	-4	6	3	359	372	-4	10	3	66	66	-4	-8	4	131	129
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9	-7	4	253	253	1	-3	4	154	-136	6	0	4	76	67	-8	4	4	107	109	5	7	4	318	321
-8	-6	4	164	168	3	-3	4	579	573	8	0	4	363	371	-6	4	4	527	550	7	7	4	85	77
-6	-6	4	481	479	5	-3	4	587	560	10	0	4	202	196	-4	4	4	213	211	9	7	4	222	220
-4	-6	4	65	67	7	-3	4	238	246	-9	1	4	112	115	-2	4	4	536	527	-6	8	4	238	240
-2	-6	4	293	285	9	-3	4	305	300	-7	1	4	407	407	0	4	4	537	514	-4	8	4	60	53
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9	-5	4	128	128	-3	-1	4	357	344	2	2	4	344	316	-8	6	4	36	35	0	10	4	203	200
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-4	-4	4	224	213	3	-1	4	747	743	8	2	4	420	428	-2	6	4	276	281	-3	11	4	45	43
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0	-4	4	798	754	7	-1	4	55	62	-9	3	4	115	118	2	6	4	218	209	1	11	4	35	34
2	-4	4	372	344	9	-1	4	260	257	-7	3	4	339	337	4	6	4	534	533	3	11	4	195	197
4	-4	4	751	734	11	-1	4	42	38	-5	3	4	382	386	6	6	4	96	101	5	11	4	169	173
6	-4	4	293	298	-10	0	4	176	184	-3	3	4	228	218	8	6	4	214	209	0	12	4	156	153
8	-4	4	204	217	-8	0	4	177	180	-1	3	4	826	796	10	6	4	152	161	2	12	4	100	104
10	-4	4	54	40	-6	0	4	593	580	1	3	4	209	196	-7	7	4	221	229	-1	-11	5	134	136
-9	-3	4	19	22	-4	0	4	88	86	3	3	4	611	580	-5	7	4	263	260	1	-11	5	155	149
-7	-3	4	280	271	-2	0	4	817	853	5	3	4	358	353	-3	7	4	79	74	3	-11	5	102	102
-5	-3	4	396	391	0	0	4	1076	1034	7	3	4	72	68	-1	7	4	416	407	-2	-10	5	43	41
-3	-3	4	456	434	2	0	4	579	523	9	3	4	284	276	1	7	4	56	55	0	-10	5	183	171

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
2	-10	5	38	44	-3	-5	5	219	206	-9	-1	5	179	185	0	2	5	708	652	-2	6	5	98	105
4	-10	5	168	181	-1	-5	5	411	410	-7	-1	5	151	149	2	2	5	116	106	0	6	5	490	491
-5	-9	5	231	243	1	-5	5	307	302	-5	-1	5	571	565	4	2	5	317	316	2	6	5	262	262
-3	-9	5	51	50	3	-5	5	154	163	-3	-1	5	332	314	6	2	5	522	514	4	6	5	265	262
-1	-9	5	217	211	5	-5	5	405	415	-1	-1	5	535	482	8	2	5	159	154	6	6	5	178	172
1	-9	5	208	210	7	-5	5	20	-15	1	-1	5	648	584	10	2	5	155	154	8	6	5	93	101
3	-9	5	31	10	9	-5	5	87	89	3	-1	5	225	237	-7	3	5	140	143	-7	7	5	107	112
5	-9	5	226	228	-8	-4	5	83	87	5	-1	5	330	325	-5	3	5	451	451	-5	7	5	291	295
7	-9	5	66	60	-6	-4	5	353	352	7	-1	5	48	38	-3	3	5	283	280	-3	7	5	90	87
-6	-8	5	215	229	-4	-4	5	524	512	9	-1	5	115	116	-1	3	5	560	548	-1	7	5	279	280
-4	-8	5	199	200	-2	-4	5	405	397	11	-1	5	128	121	1	3	5	440	396	1	7	5	306	301
-2	-8	5	183	182	0	-4	5	680	639	-8	0	5	119	113	3	3	5	131	126	3	7	5	176	171
0	-8	5	576	569	2	-4	5	373	337	-6	0	5	378	393	5	3	5	348	337	5	7	5	210	197
2	-8	5	163	165	4	-4	5	422	429	-4	0	5	538	515	7	3	5	73	66	7	7	5	63	70
4	-8	5	115	115	6	-4	5	253	253	-2	0	5	572	502	9	3	5	108	103	9	7	5	139	139
6	-8	5	207	200	8	-4	5	64	-63	0	0	5	921	890	-8	4	5	122	131	-6	8	5	182	182
8	-8	5	60	59	10	-4	5	191	192	2	0	5	185	165	-6	4	5	338	345	-4	8	5	245	250
-7	-7	5	96	99	-7	-3	5	142	142	4	0	5	262	250	-4	4	5	330	326	-2	8	5	177	179
-5	-7	5	265	266	-5	-3	5	566	587	6	0	5	449	434	-2	4	5	285	286	0	8	5	277	273
-3	-7	5	94	90	-3	-3	5	212	205	8	0	5	105	109	0	4	5	601	573	2	8	5	144	145
-1	-7	5	411	412	-1	-3	5	238	215	10	0	5	174	168	2	4	5	278	247	4	8	5	261	258
1	-7	5	449	438	1	-3	5	576	505	-9	1	5	173	179	4	4	5	405	396	6	8	5	155	154
3	-7	5	68	63	3	-3	5	454	422	-7	1	5	143	144	6	4	5	257	256	8	8	5	71	66
5	-7	5	286	281	5	-3	5	527	527	-5	1	5	395	395	8	4	5	66	68	-5	9	5	255	263
7	-7	5	155	162	7	-3	5	168	167	-3	1	5	200	175	10	4	5	244	239	-3	9	5	173	186
9	-7	5	177	182	9	-3	5	215	224	-1	1	5	733	641	-7	5	5	195	204	-1	9	5	213	215
-6	-6	5	184	189	-8	-2	5	68	64	1	1	5	525	456	-5	5	5	326	321	1	9	5	123	123
-4	-6	5	163	156	-6	-2	5	357	348	3	1	5	51	51	-3	5	5	62	56	3	9	5	147	150
-2	-6	5	86	81	-4	-2	5	389	368	5	1	5	714	693	-1	5	5	409	411	5	9	5	263	263
0	-6	5	376	371	-2	-2	5	154	-140	7	1	5	485	491	1	5	5	490	465	7	9	5	84	84
2	-6	5	70	63	0	-2	5	351	315	9	1	5	200	199	3	5	5	316	315	-2	10	5	84	88
4	-6	5	251	256	2	-2	5	474	433	11	1	5	136	134	5	5	5	419	417	0	10	5	182	177
6	-6	5	282	280	4	-2	5	477	473	-8	2	5	64	64	7	5	5	128	130	2	10	5	76	74
8	-6	5	110	116	6	-2	5	322	326	-6	2	5	290	278	9	5	5	193	195	4	10	5	203	205
-7	-5	5	133	141	8	-2	5	135	142	-4	2	5	283	271	-6	6	5	292	298	-1	11	5	137	138
-5	-5	5	341	326	10	-2	5	270	268	-2	2	5	277	268	-4	6	5	154	157	1	11	5	154	158

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
3	11	5	89	94	9	-5	6	107	106	-6	0	6	223	232	-6	4	6	132	133	-3	9	6	141	145
0	-10	6	137	151	-6	-4	6	207	212	-6	0	6	201	201	-4	4	6	483	491	-1	9	6	50	43
2	-10	6	154	169	-4	-4	6	521	516	-4	0	6	632	611	-2	4	6	114	116	1	9	6	293	296
-3	-9	6	147	147	-2	-4	6	157	153	-2	0	6	295	273	0	4	6	388	369	3	9	6	142	144
-1	-9	6	87	96	0	-4	6	483	466	0	0	6	456	415	2	4	6	388	373	5	9	6	181	181
1	-9	6	164	179	2	-4	6	363	345	2	0	6	258	231	4	4	6	109	107	0	10	6	136	139
3	-9	6	84	83	4	-4	6	99	106	4	0	6	236	225	6	4	6	303	298	2	10	6	161	167
5	-9	6	155	151	6	-4	6	202	196	6	0	6	383	379	8	4	6	123	128	0	-8	7	41	44
-4	-8	6	268	274	8	-4	6	66	70	10	0	6	151	155	-5	5	6	183	191	2	-8	7	255	251
-2	-8	6	184	189	-7	-3	6	127	133	-7	1	6	39	32	-3	5	6	256	259	4	-8	7	117	116
0	-8	6	251	257	-5	-3	6	340	334	-5	1	6	306	291	-1	5	6	199	201	-3	-7	7	278	283
2	-8	6	114	105	-3	-3	6	153	138	-3	1	6	416	398	1	5	6	588	574	-1	-7	7	84	80
4	-8	6	124	117	-1	-3	6	243	220	-1	1	6	203	184	3	5	6	184	187	1	-7	7	154	165
6	-8	6	214	209	1	-3	6	770	711	1	1	6	487	452	5	5	6	300	292	3	-7	7	207	211
-5	-7	6	207	213	3	-3	6	161	166	3	1	6	353	342	7	5	6	251	255	5	-7	7	100	112
-3	-7	6	263	261	5	-3	6	319	336	5	1	6	708	711	9	5	6	117	113	-4	-6	7	194	204
-1	-7	6	217	216	7	-3	6	250	255	7	1	6	241	235	-6	6	6	31	37	-2	-6	7	192	184
1	-7	6	310	294	9	-3	6	133	144	9	1	6	48	45	-4	6	6	258	267	0	-6	7	69	76
3	-7	6	67	67	-6	-2	6	124	119	-6	2	6	50	51	-2	6	6	131	132	2	-6	7	260	270
5	-7	6	246	261	-4	-2	6	239	231	-4	2	6	458	464	0	6	6	392	399	4	-6	7	98	108
7	-7	6	194	197	-2	-2	6	85	-85	-2	2	6	132	132	2	6	6	230	231	6	-6	7	180	187
-6	-6	6	33	33	0	-2	6	653	612	0	2	6	341	310	6	6	6	289	289	-5	-5	7	116	129
-4	-6	6	313	312	2	-2	6	466	442	2	2	6	351	330	8	6	6	102	106	-3	-5	7	264	264
-2	-6	6	67	63	4	-2	6	105	120	4	2	6	325	324	-5	7	6	200	209	-1	-5	7	90	83
0	-6	6	258	259	6	-2	6	385	395	6	2	6	419	413	-3	7	6	193	194	1	-5	7	240	236
2	-6	6	226	219	8	-2	6	143	143	8	2	6	24	-15	-1	7	6	135	138	3	-5	7	232	217
4	-6	6	128	143	10	-2	6	153	155	10	2	6	151	155	1	7	6	339	332	5	-5	7	70	68
6	-6	6	277	287	-7	-1	6	122	128	-7	3	6	78	79	3	7	6	74	-71	7	-5	7	224	227
8	-6	6	134	134	-5	-1	6	404	395	-5	3	6	420	418	5	7	6	134	134	-4	-4	7	246	254
-5	-5	6	312	313	-3	-1	6	310	297	-3	3	6	384	400	7	7	6	182	191	-2	-4	7	312	291
-3	-5	6	289	284	-1	-1	6	254	246	-1	3	6	87	86	-4	8	6	256	265	0	-4	7	155	152
-1	-5	6	94	101	1	-1	6	610	568	1	3	6	440	406	-2	8	6	52	48	2	-4	7	347	333
1	-5	6	394	385	3	-1	6	36	-22	3	3	6	32	32	0	8	6	245	251	4	-4	7	91	80
3	-5	6	114	115	5	-1	6	206	200	5	3	6	190	177	2	8	6	235	236	6	-4	7	152	158
5	-5	6	179	177	7	-1	6	141	131	7	3	6	120	111	4	8	6	74	74	8	-4	7	177	175
7	-5	6	127	118	9	-1	6	70	70	9	3	6	84	87	6	8	6	233	235	-5	-3	7	38	42

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-3	-3	7	396	378	-3	1	7	403	380	-1	5	7	229	230	-3	-3	8	308	315	0	2	8	157	159
-1	-3	7	301	277	-1	1	7	100	91	1	5	7	328	323	-1	-3	8	172	167	2	2	8	274	271
1	-3	7	276	286	1	1	7	450	453	3	5	7	249	244	1	-3	8	89	98	4	2	8	118	110
3	-3	7	273	263	3	1	7	567	561	5	5	7	172	176	3	-3	8	275	270	6	2	8	79	85
5	-3	7	116	128	5	1	7	109	116	7	5	7	221	218	5	-3	8	86	86	-3	3	8	172	173
7	-3	7	259	265	7	1	7	173	177	-4	6	7	216	230	-4	-2	8	159	168	-1	3	8	200	200
-6	-2	7	18	-14	9	1	7	101	105	-2	6	7	254	267	-2	-2	8	351	345	1	3	8	61	53
-4	-2	7	173	170	-6	2	7	99	104	0	6	7	84	86	0	-2	8	23	16	3	3	8	235	223
-2	-2	7	434	403	-4	2	7	273	281	2	6	7	144	138	2	-2	8	231	233	5	3	8	77	79
0	-2	7	219	220	-2	2	7	203	185	4	6	7	118	120	4	-2	8	210	208	-2	4	8	312	329
2	-2	7	311	309	0	2	7	148	149	6	6	7	207	206	6	-2	8	125	137	0	4	8	86	91
4	-2	7	140	137	2	2	7	514	500	-3	7	7	232	247	-3	-1	8	269	272	2	4	8	202	199
6	-2	7	236	243	4	2	7	184	170	-1	7	7	70	71	-1	-1	8	184	164	4	4	8	189	192
8	-2	7	199	199	6	2	7	102	100	1	7	7	60	46	1	-1	8	82	74	6	4	8	75	76
-5	-1	7	108	110	8	2	7	172	177	3	7	7	97	101	3	-1	8	266	263	-1	5	8	203	220
-3	-1	7	406	394	-5	3	7	175	189	5	7	7	145	153	5	-1	8	106	105	1	5	8	93	97
-1	-1	7	175	167	-3	3	7	242	243	0	8	7	117	124	7	-1	8	171	184	3	5	8	290	296
1	-1	7	219	203	-1	3	7	53	44	2	8	7	213	216	-4	0	8	88	96	5	5	8	68	68
3	-1	7	213	193	1	3	7	252	245	4	8	7	112	121	-2	0	8	302	283	0	6	8	45	-44
5	-1	7	43	48	3	3	7	178	157	0	-6	8	31	31	0	0	8	142	122	2	6	8	206	207
7	-1	7	256	254	5	3	7	26	27	2	-6	8	166	184	2	0	8	283	277	4	6	8	197	203
9	-1	7	88	91	7	3	7	239	239	4	-6	8	144	144	4	0	8	123	119	2	-2	9	91	100
-6	0	7	142	141	-4	4	7	226	238	-1	-5	8	164	157	6	0	8	112	118	1	-1	9	74	73
-4	0	7	365	366	-2	4	7	205	196	1	-5	8	127	134	-3	1	8	222	224	3	-1	9	174	191
-2	0	7	289	258	0	4	7	211	211	3	-5	8	241	242	-1	1	8	298	286	0	0	9	190	179
0	0	7	88	81	2	4	7	344	332	5	-5	8	71	73	1	1	8	269	275	2	0	9	43	52
2	0	7	464	441	4	4	7	96	99	-2	-4	8	288	284	3	1	8	278	282	4	0	9	221	224
4	0	7	158	154	6	4	7	225	227	0	-4	8	94	92	7	1	8	191	195	1	1	9	70	74
6	0	7	106	116	8	4	7	159	162	2	-4	8	251	250	-4	2	8	45	47	3	1	9	109	123
8	0	7	193	197	-5	5	7	100	103	4	-4	8	142	140	-2	2	8	320	317	2	2	9	53	53
-5	1	7	174	176	-3	5	7	320	331	6	-4	8	86	91										

DEVIATIONS GREATER THAN 2 SIGMA

H	K	L	FO	FC	D/SIGMA
2	0	0	67.88	77.24	2.37
-3	1	0	8.25	6.69	3.25
-1	1	0	116.44	142.62	3.87
1	1	0	119.62	141.76	3.18
5	1	0	80.40	92.92	2.68
-1	3	0	86.49	101.53	2.99
1	3	0	75.35	85.40	2.29
5	3	0	87.24	99.93	2.50
-4	4	0	86.93	99.35	2.45
0	4	0	124.32	140.00	2.17
4	4	0	90.11	101.61	2.19
-8	10	0	6.26	5.47	2.07
-3	11	0	8.25	7.05	2.47
-1	-11	1	3.89	2.25	6.31
3	-9	1	9.63	11.44	3.21
4	-8	1	2.73	2.10	3.20
1	-5	1	73.52	82.67	2.14
9	-5	1	4.80	3.80	3.36
-4	-4	1	79.61	91.59	2.59
2	-4	1	95.08	107.85	2.31
-2	-2	1	9.09	7.51	2.98
2	-2	1	72.11	85.18	3.12
-4	0	1	116.12	130.64	2.15
-2	0	1	180.26	208.79	2.72
-3	1	1	88.78	100.10	2.19
-1	1	1	69.68	78.21	2.10
5	1	1	85.33	97.47	2.44
2	2	1	88.68	101.52	2.49
5	3	1	2.52	3.07	3.03
-4	4	1	84.68	99.48	3.00
-3	5	1	3.21	3.84	3.11
1	5	1	107.56	120.28	2.03
9	7	1	1.33	1.01	2.23
-7	9	1	2.30	1.69	3.01
-6	10	1	7.33	8.36	2.35
3	11	1	4.56	2.99	5.43
9	-7	2	4.97	4.21	2.47
2	-4	2	106.78	119.87	2.11
2	-2	2	123.90	140.55	2.31
4	-2	2	8.93	10.05	2.15
-1	-1	2	34.08	26.50	3.82
-4	0	2	131.42	148.11	2.18
0	0	2	44.26	36.28	3.10
-1	1	2	9.54	7.55	3.57
-3	3	2	80.12	93.35	2.84
-2	4	2	86.15	98.42	2.45
4	4	2	19.22	16.98	2.00
0	-2	3	48.62	42.82	2.05
2	-2	3	11.72	13.65	2.83
3	-1	3	73.96	83.14	2.13
1	11	3	1.80	1.45	2.26
10	-4	4	5.40	3.95	4.36
2	-2	4	20.42	16.95	2.92

6	2	4	3.91	3.21	2.83
2	-10	5	3.81	4.44	2.37
3	-9	5	3.08	0.99	7.93
7	-5	5	1.99	1.50	5.00
1	-3	5	57.60	50.47	2.13
7	-1	5	4.76	3.81	3.30
-2	0	5	57.21	50.20	2.10
-3	1	5	19.95	17.55	2.07
-1	1	5	73.27	64.14	2.14
1	1	5	52.54	45.57	2.28
4	-6	6	12.79	14.33	2.05
4	-2	6	10.54	12.00	2.38
3	-1	6	3.55	2.21	5.65
-7	1	6	3.91	3.18	2.80
8	2	6	2.44	1.47	4.75
-6	6	6	3.13	3.68	2.20
-1	9	6	5.01	4.35	2.11
5	-7	7	10.04	11.24	2.02
4	-4	7	9.13	7.97	2.16
-1	3	7	5.26	4.40	2.67
3	3	7	17.77	15.68	2.02
1	7	7	6.01	4.64	3.75
0	-2	8	2.34	1.59	4.46
0	0	8	14.18	12.15	2.45
1	3	8	6.09	5.27	2.20
2	0	9	4.35	5.23	3.08
3	1	9	10.86	12.30	2.26

Appendix III. Listing of Data Reduction Programme

```
                                                    104
  111 ZM=M                                                                  00007800
      STD1=STD2                                                             00007900
      STD2=RAW                                                              00008000
      FACT1=STD1/STDRD                                                      00008100
      SLOPE=(STD2-STD1)/ZM                                                  00008200
      REFL=1.0                                                              00008300
      REWIND 10                                                             00008400
   99 READ(10,300) H,J,K,CODE,NPI,BGL,INT,BGR,RAW,TWTHET,LP,WIDTH           00008500
      IF(CODE.IS."I") GO TO 87                                              00008600
      FACTOR=FACT1*(1.0+SLOPE*REFL/STD1)                                    00008700
      ATTEN=1.0                                                             00008800
      IF(NPI.LE.0.0)ATTEN=13.1                                              00008900
      STUFF=(RAW*WIDTH*ATTEN)/(LP*FACTOR*ABS(NPI))                          00009000
      REFL=REFL+1.0                                                         00009100
      IF(STUFF.GT.0.0) GO TO 1000                                           00009200
      F=0.01                                                                00009600
      SIGF=10000                                                            00009700
      GO TO 301                                                             00009800
 1000 F=SQRT(STUFF)                                                         00009900
      SIGF=0.5*SQRT((INT+4*(BGL+BGR))*WIDTH*ATTEN/(LP*FACTOR*ABS(NPI)*RA00010000
     1 W))                                                                  00010100
      NOBS=NOBS+1                                                           00010300
  301 WRITE(6,9) H,J,K,INT,BGL,BGR,RAW,NPI,FACTOR,F,SIGF,LP,WIDTH,ATTEN     00010400
    9 FORMAT(1H ,3I5,4F10.0,F6.0,F10.5,2F10.3,F10.4,2F7.2,                  00010500
     1F10.5)                                                                00010600
      N=1                                                                   00010700
      WRITE(8,15) H,J,K,F,SIGF,N                                            00010800
   15 FORMAT(3I4,2F8.2,I4)                                                  00010900
      GO TO 99                                                              00011000
  800 WRITE(8,444)                                                          00011100
  444 FORMAT('                                                  ')          00011200
      WRITE(6,11) NOBS                                                      00011500
   11 FORMAT(7HONOBS=  I6)                                                  00011600
      STOP                                                                  00011700
      END                                                                   00011800
```

DATE 10/01/81 TIME IS 11:24

SYSTEM/DUMPALL VERSION 3.1.242

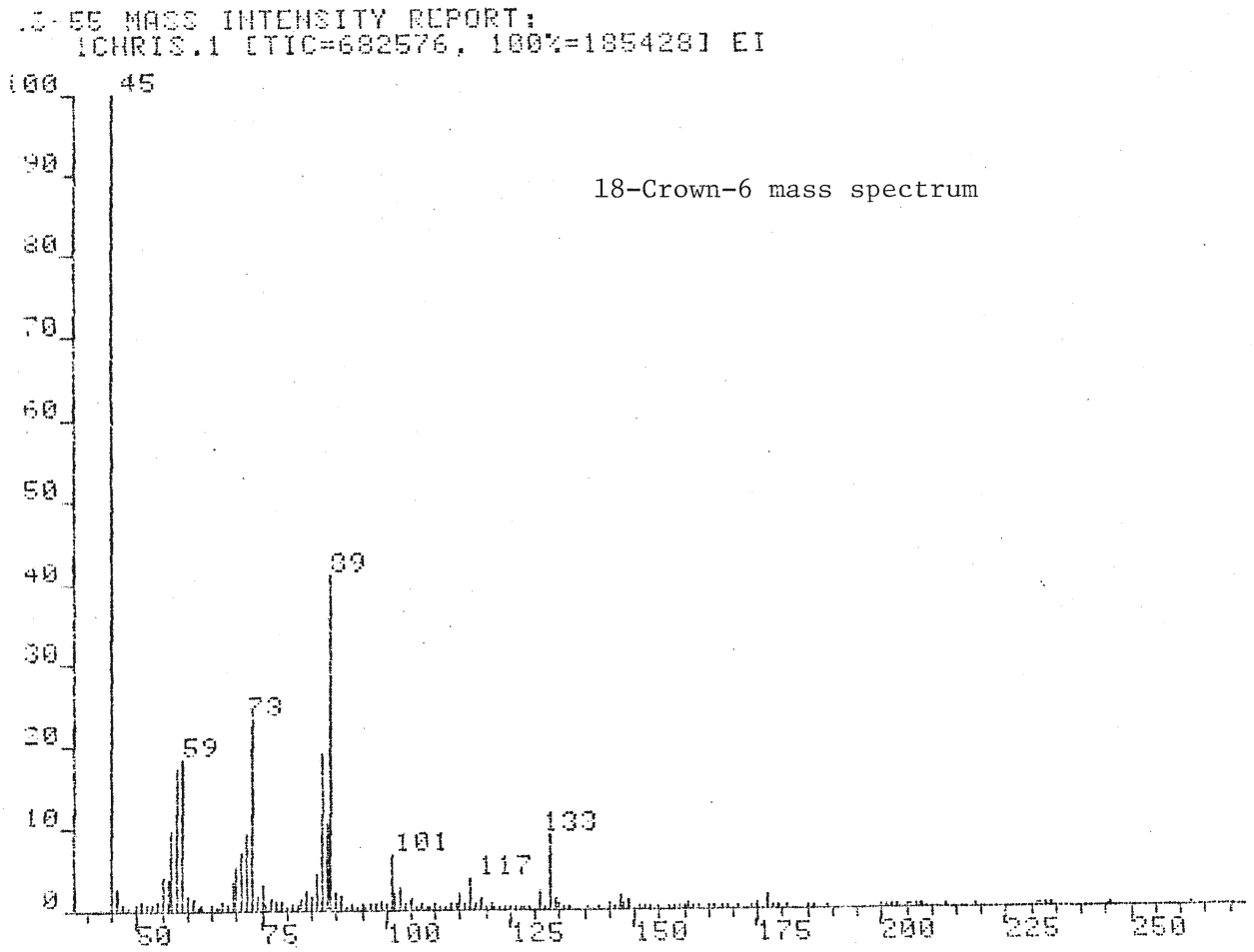
MAXRECSIZEIN = 14 BLOCKSIZEIN = 14
*** EBCDIC *** UNITS=WORDS

```
 0          DIMENSION TITLE(6)                                                    00000100
 1          REAL J,K,L,LP,INT,NPI,ATTEN                                           00000200
 2          PI=ARCOS(-1.)                                                         00000300
 3          READ(5,150) TITLE                                                     00000800
 4   150    FORMAT(8X,6A6)                                                        00000900
 5          WRITE(6,155) TITLE                                                    00001000
 6   155    FORMAT(1H0,12A6)                                                      00001100
 7          NOBS=0                                                                00001200
 8   10     READ(5,101,END=88) IDENT                                              00001300
 9   101    FORMAT(I2)                                                            00001400
10          IF(IDENT.NE.1) GO TO 39                                               00001500
11          BACKSPACE 5                                                           00001600
12          READ(5,200)  H,J,K,CODE,NPI,BGL,INT,BGR                               00001700
13   200    FORMAT(8X,3I5,X,A6,7X,I4,I6,I7,I6)                                    00001800
14          GO TO 10                                                              00001900
15       39 IF(IDENT.NE.2) GO TO 10                                               00002000
16          BACKSPACE 5                                                           00002100
17          READ(5,500) THETA,WIDTH                                               00002200
18   500    FORMAT(8X,F8.3,27X,F7.3)                                              00002300
19          WIDTH=ABS(WIDTH)                                                      00002600
20          TWTHET=2*THETA*(PI/180)                                               00002700
21          THET=TWTHET/2                                                         00002800
22          L=1/(SIN(TWTHET))                                                     00002900
23          PFACT=((COS(12.2*PI/180))**2+(COS(TWTHET))**2)/(1+(COS(12.2*PI/18000003000
24         1))**2)                                                                00003100
25          LP=L*PFACT                                                            00003300
26          RAW=INT-2*(BGL+BGR)                                                   00003400
27          WRITE(9,300)H,J,K,CODE,NPI,BGL,INT,BGR,RAW,TWTHET,LP,WIDTH            00005000
28    300   FORMAT(3I5,A1,F6.0,4F10.1,3F10.5)                                     00005100
29          GO TO 10                                                              00005300
30       88 WRITE(9,1)                                                            00005400
31    1     FORMAT(17X,'    ',92X)                                                00005500
32          REWIND 9                                                              00005800
33          READ(9,76)STORD                                                       00005900
34   76     FORMAT(52X,F10.0,30X)                                                 00006000
35          STO2=STORD                                                            00006300
36    87    M=1                                                                   00006400
37          M=M+1                                                                 00006500
38          REWIND 10                                                             00006600
39          WRITE(6,20)                                                           00006700
40    20    FORMAT(1H0,4X,'H',4X,'K',4X,'L',7X,'INT',7X,'BGL',7X,'BGR',           00006800
41         1 7X,'RAW',3X,'NPI',4X,'FACTOR',9X,'F',6X,'SIGF',8X,'LP',2X,           00006900
42         2 'WIDTH',2X,'ATTEN')                                                  00007000
43   199    READ(9,300)H,J,K,CODE,NPI,BGL,INT,BGR,RAW,TWTHET,LP,WIDTH             00007100
44    600   FORMAT(3I5,2X,A1,11X,3F10.0,13X,F10.5,12X,F10.0)                      00007200
45          IF(CODE.IS." ") GO TO 800                                             00007300
46          WRITE(10,300) H,J,K,CODE,NPI,BGL,INT,BGR,RAW,TWTHET,LP,WIDTH          00007400
47          IF(CODE.IS."I") GO TO 111                                             00007500
48          M=M+1                                                                 00007600
49          GO TO 199                                                             00007700
```

Appendix IV. Mass and NMR Spectra including experimental details.

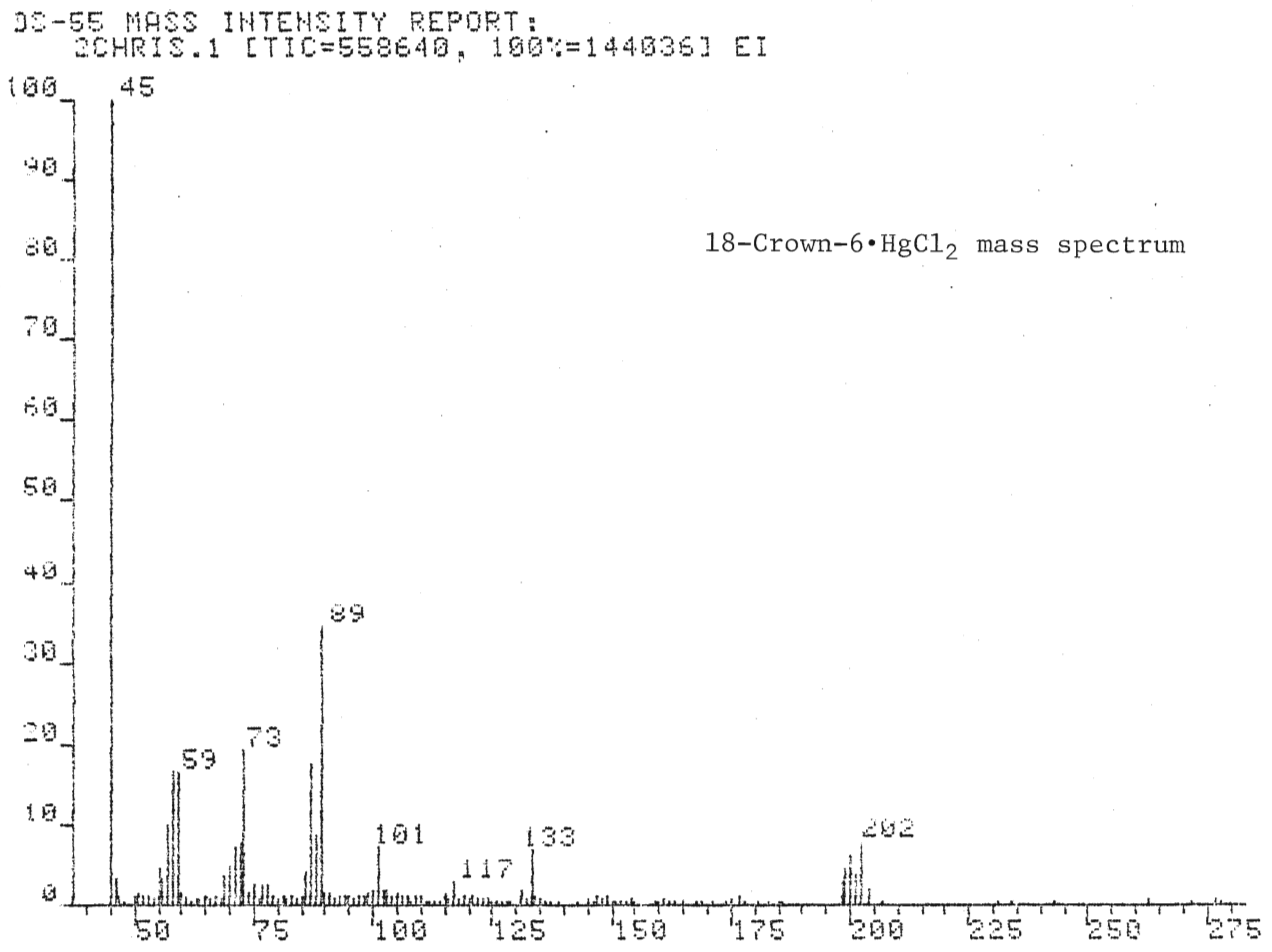
Routine ^{13}C and ^{1}H NMR spectra were obtained for the 18-crown-6 and each of the complexes. The solvent used in each case was deuterochloroform, with TMS as internal standard, and the spectra were obtained on a Bruker WP-60 spectrometer. The appropriate instrumental settings and constants are recorded on each spectrum.

Routine electron-impact mass spectra were obtained for the same materials using an AEI MS-30 double beam mass spectrometer.



18-Crown-6 mass spectrum

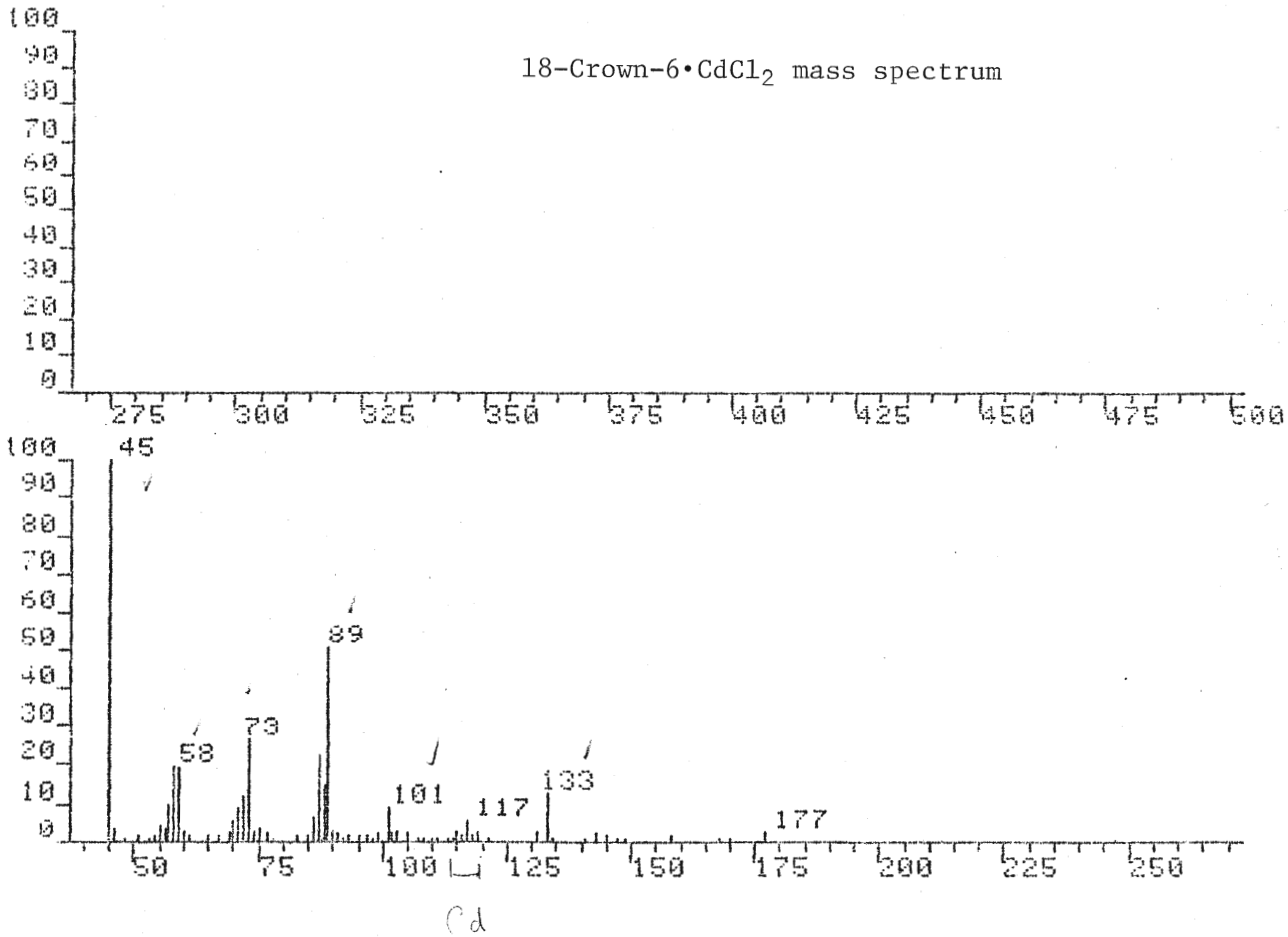
II



18-Crown-6•$HgCl_2$ mass spectrum

R

18-Crown-6•$CdCl_2$ mass spectrum



R

Cd

No

BRUKER
SPECTROSPIN

C. Paige

60 MHz - ^{1}H - Spectrum

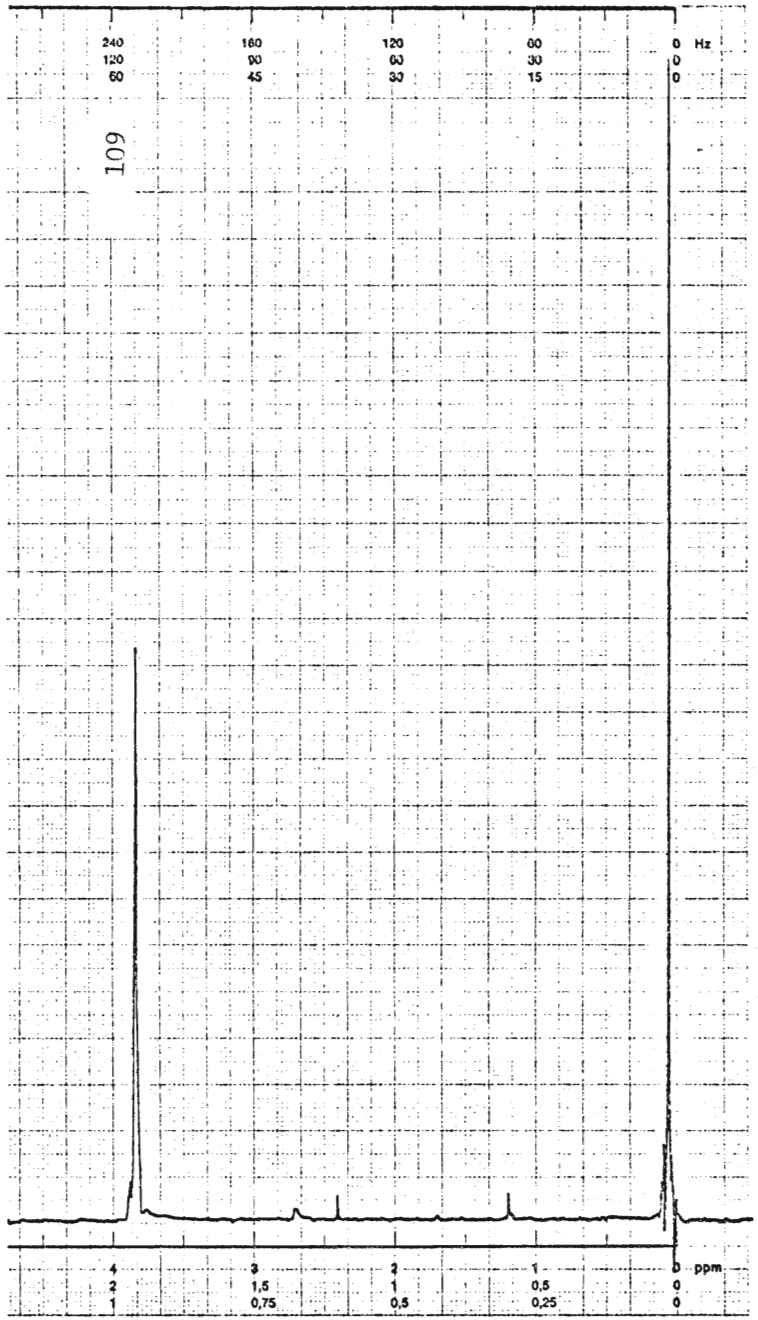
Sample Cadmium

Conc. ____ % in $CDCl_3$

Int. Standard TMS

Temp. amb. ☒

____ °K ☐



Signal f_1

Puls width (PW) 1.3 µsec

Points (SI) 0 k/ 4 k

Spectrum f_2

width (SW) f_1 750 Hz/cm

Offset (A) f_1 2625 Hz

Time 5.5 sec

times (NS) 4 scans

Time constant (TC) ____

Decoupling f_3

Frequency ____ Hz

Power ____

Date 11/13/81

Operator [signature]

^{1}H NMR spectra for 18-crown-6•$CdCl_2$ and 18-crown-6•$HgCl_2$

221.246 3.687 72.221 11.571
219.964 3.666 82.075 8.209
0.000 0.000 57.433 8.366

No 2

BRUKER
SPECTROSPIN

C. PAIGE

60 MHz - ^{1}H - Spectrum

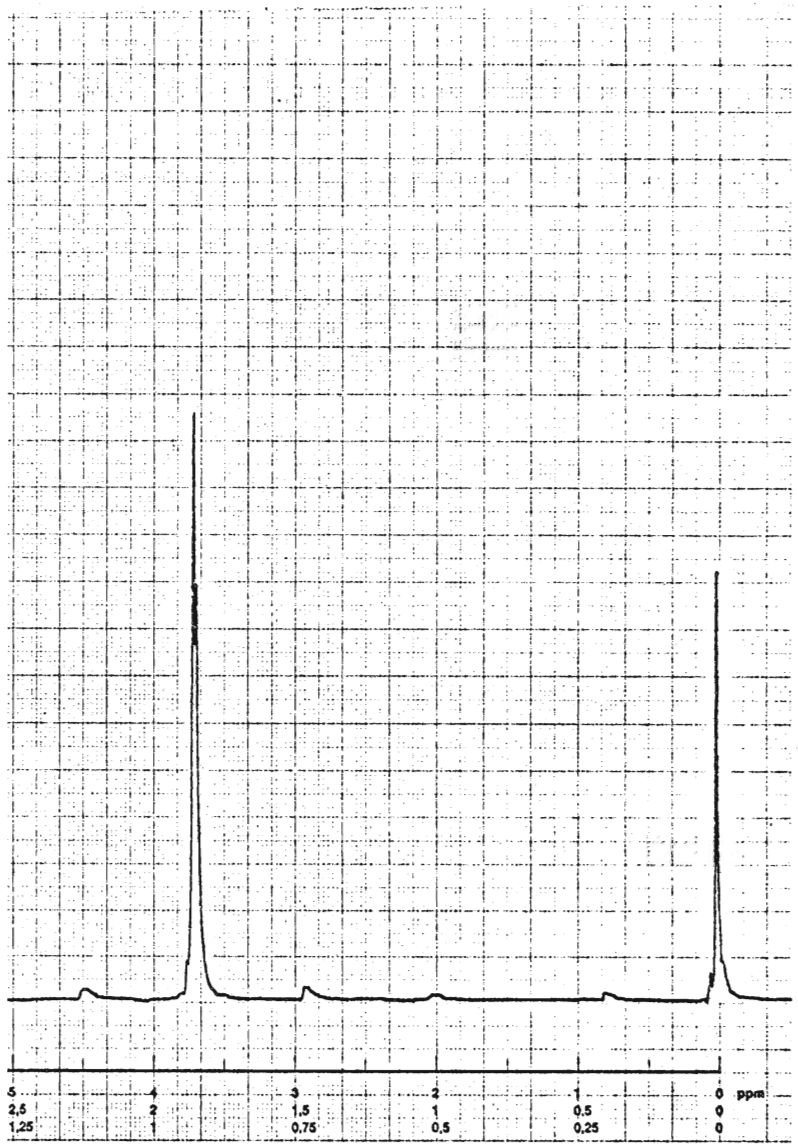
Sample 18-CROWN-6 (Hg)

Conc. ____ % in $CDCl_3$

Int. Standard TMS

Temp. amb. ☒

____ °K ☐



Signal f_1

Puls width (PW) 1.3 µsec

Points (SI) 8 k/ 4 k

Spectrum f_2

width (SW) f_1 750 Hz/cm

Offset (A) f_1 2625 Hz

Time 5.5 sec

times (NS) 16 scans

Time constant (TC) ____

Decoupling f_3

Frequency ____ Hz

Power ____

Date 6/26/81

Operator [signature]

No. 2

BRUKER
SPECTROSPIN

A/C 110

15,08 MHz-^{13}C-Spectrum

Sample 18 Crown-6 + $HgCl_2$

Conc. ... % in $CDCl_3$

Int. Standard TMS

Temp. amb. ☒

... °K ☐

1875 Hz. Rel.

Signal f$_1$

Puls width (PW) 3.3 µsec

Points (SI) 8 k 4 k

Spectrum

width (SW) f$_2$ 3750 Hz cm

Offset (A) f$_2$ 6200 Hz

Time 1.1 sec

times (NS) 5342 scans

Time constant (TC) 0.5

Decoupling f$_2$

Frequency 2600 Hz

BB ☒ 5W/6

off Res ☐

gated ☐

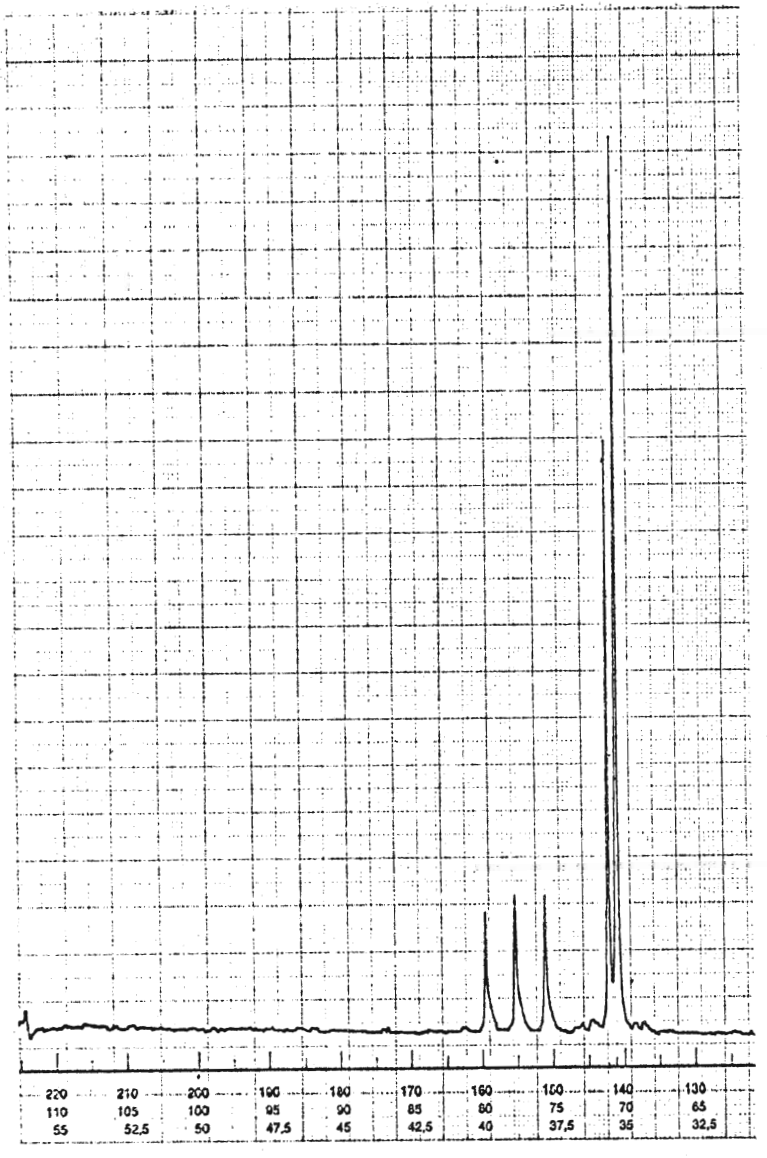
Date 7/3/81

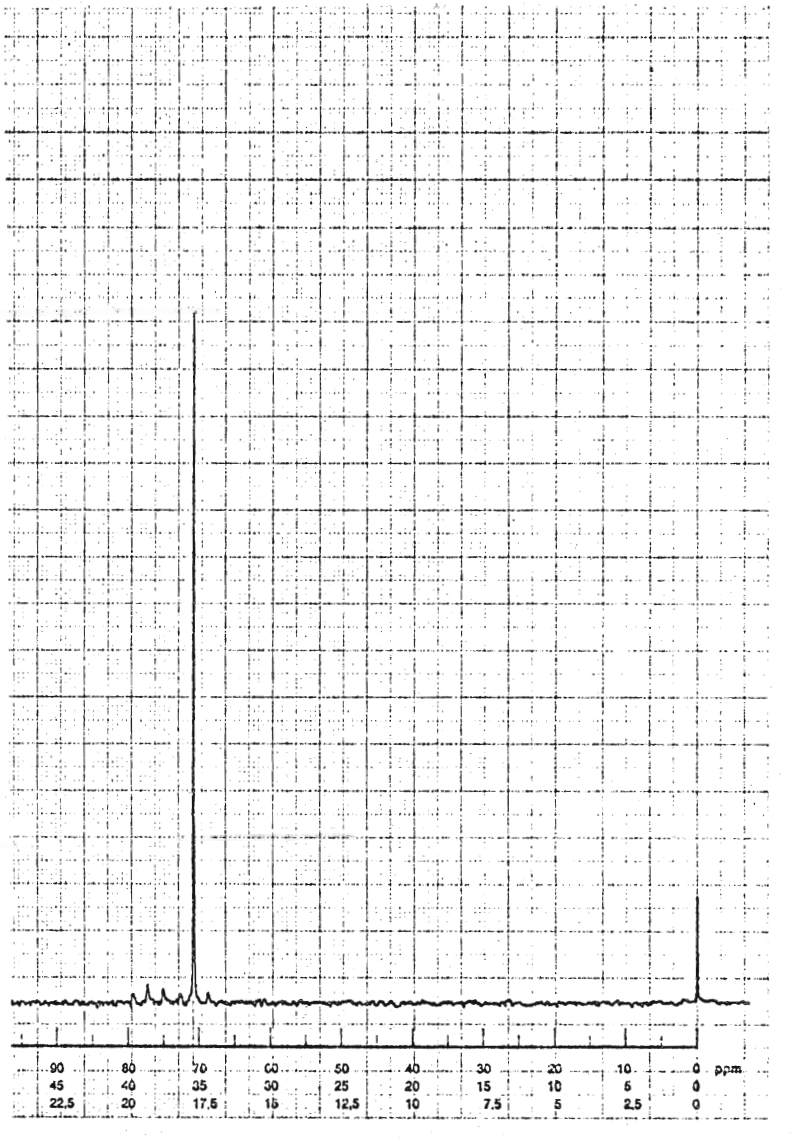
Operator

1	1066.509	70.723	15368.660	5958.439
	1057.330	70.114	27118.141	8971.082
	0.000	0.000	9856.895	3460.662

1	1066.509	70.723	1031.785	436.390
2	0.000	0.000	126.882	67.917

^{13}C NMR spectra for 18-crown-6 and 18-crown-6•$HgCl_2$





15,08 MHz-^{13}C-Spectrum

Sample 18-Crown-6 + $HgCl_2$

Conc. ... % in $CDCl_3$

Int. Standard TMS

Temp. amb. ☒

... °K ☐

Signal f$_1$

Puls width (PW) 3.3 µsec

Points (SI) 8 k 4 k

Spectrum

width (SW) f$_2$ 3750 Hz cm

Offset (A) f$_2$ 6200 Hz

Time 1.1 sec

times (NS) 200 scans

Time constant (TC) 0.5

Decoupling f$_2$

Frequency 2600 Hz

BB ☒ 5W/6

off Res ☐

gated ☐

Date 7/2/81

Operator

No 1

BRUKER SPECSPIN 111

C Paige

15,08 MHz - ^{13}C - Spectrum

Sample 18-crown6-$HgCl_2$

Conc. ____ % in $CDCl_3$

Int. Standard TMS

Temp. amb. ☒

____ °K ☐

1875 Hz. Rot.

Signal f_1

Puls width (PW) 33 µsec

Points (SI) 8 k/ 4 k

Spectrum

width (SW) f_1 3750 Hz/cm

Offset (A) f_1 6200 Hz

Time 1.1 sec

times (NS) 3,000 scans

Time constant (TC) 0.5

Decoupling f_2

Frequency 2600 Hz

BB ☒ 54/6

off Res ☐

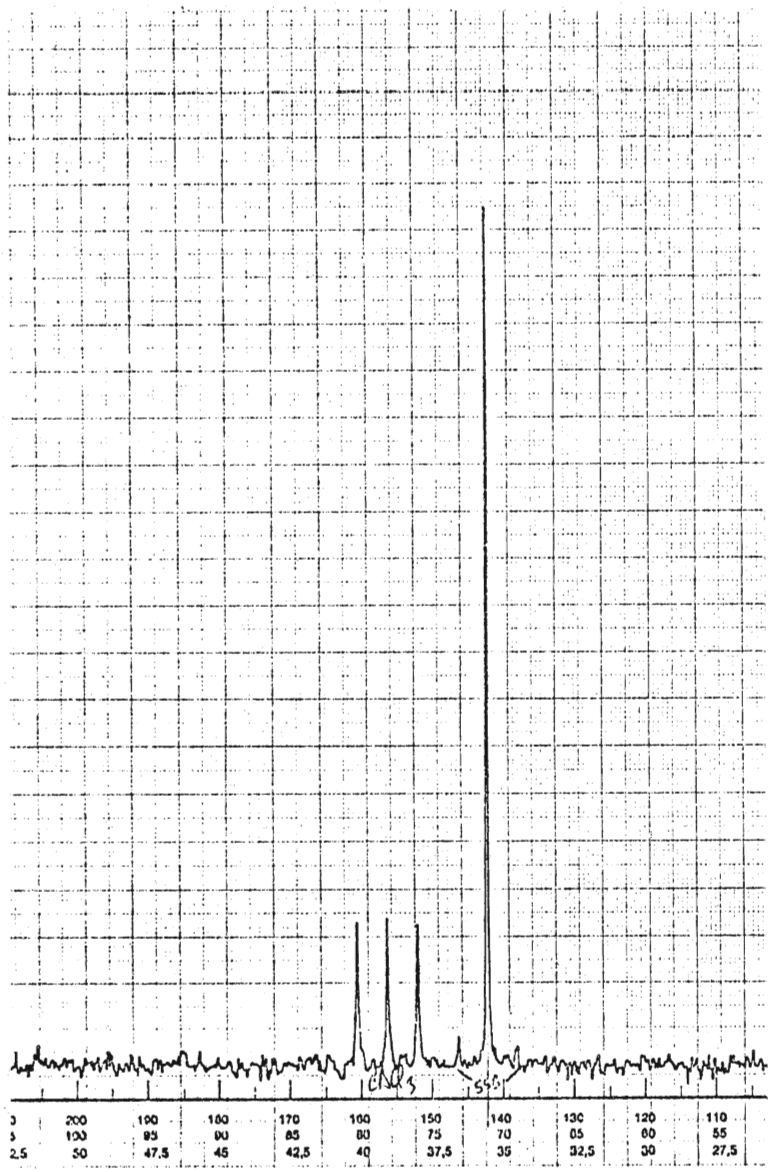
gated ☐

Date 11/18/81

Operator J

70.175 1357.622 539.671
0.000 811.116 450.463

^{13}C NMR spectra for 18-crown-6·$HgCl_2$, with and without excess 18-crown-6



No 2

BRUKER SPECTROSPIN

C Paige

15,08 MHz - ^{13}C - Spectrum

Sample 18-crown-6·$HgCl_2$ + excess 18-crown-6

Conc. ____ % in $CDCl_3$

Int. Standard TMS

Temp. amb. ☒

____ °K ☐

Signal f_1

Puls width (PW) 33 µsec

Points (SI) 8 k 4 k

Spectrum

width (SW) f_1 3750 Hz/cm

Offset (A) f_1 6200 Hz

Time 1.1 sec

times (NS) 2600 scans

Time constant (TC) 0.5

Decoupling f_2

Frequency 2600 Hz

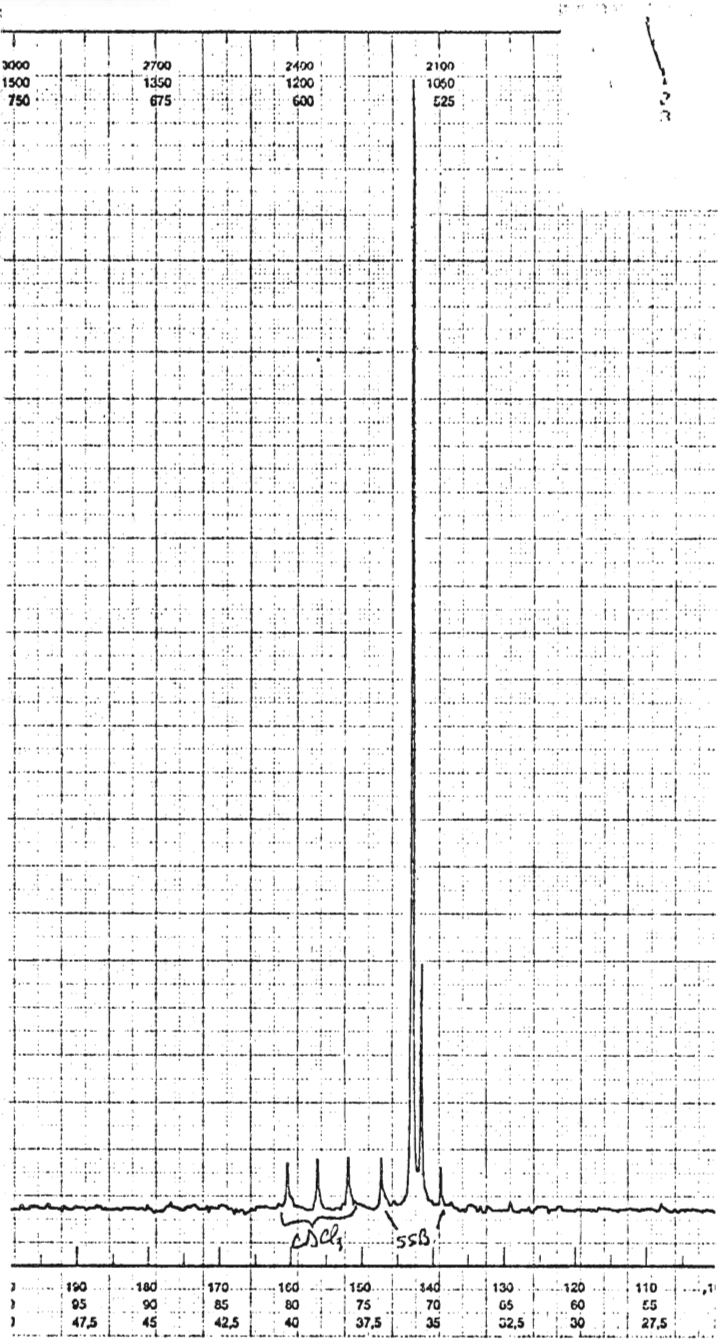
BB ☒ 54/6

off Res ☐

gated ☐

Date 11/18/81

Operator J



Appendix V

Attempts to prepare various metal-crown complexes

Investigations initially centred around attempts to make complexes of the crown-ether, dibenzo-18-Crown-6 with $HgCl_2$, $CdCl_2$ and methyl mercury iodide.

Solutions of dibenzo-18-Crown-6 in hot 1-butanol, were mixed with $HgCl_2$ dissolved in hot methanol or hot 1-butanol. Difficulty was experienced in avoiding the rapid production of a flocculent mass after a few minutes of cooling. This was presumably the sparingly-soluble dibenzo 18-Crown-6 coming out of solution, mixed with any product complex. By reducing the concentration of the crown ether and cooling the solutions in ice before mixing, it proved possible to obtain needle-like crystals of a product which gave the following analysis:

	C	H	O	Cl	Hg
Theory (%)	38	3.8	15.19	11.2	31.7
Experiment (%)	38.25	3.84	14.90	10.5	31.7

(Micronanalytisches Laboratorium, Bonn)

Powder photographs of the starting materials were compared to a sample of the potential complex and new diffraction lines were observed. With the elemental analysis and powder data evidence, it was felt that a new complex had been produced. Polarizing microscope observations suggested that many of the crystals were disordered in that they did not give sharp extinctions between crossed polars. Nevertheless, a crystal was found which seemed acceptable, and this was subjected to X-ray diffractometry on a Picker 4-circle manual diffractometer. The decay in the intensity of a standard

reflection (∿30%) and the change in colour of the crystal were taken as evidence of crystal decomposition. Attempts at refinement of the data led nowhere.

At a later date, a new crystal was again submitted to X-ray diffractometry on a new Enraf-Nonius DAC-4 diffractometer. This time there was no evidence of crystal decomposition. Again, however, attempts to refine the structure led nowhere. It is believed that the crystal is probably disordered. A later attempt may be made to repeat the synthesis using an alternative solvent. Various researchers (55) have reported synthesis of Hg and Cd diaza-crown ether complexes from acetonitrile, an observation possibly worth pursuing.

Effort then shifted to attempting to prepare complexes of dibenzo-18-Crown-6 with $CdCl_2$ and methyl mercury iodide. Both of these gave a product but in neither case did the reaction produce good crystalline results. The $CdCl_2$ adduct produced was subjected to oscillation photography, when it was immediately apparent that the material was highly disordered. The investigation was stopped.

For completeness, it should be mentioned that the MeHgI product was submitted for microanalysis, when <0.5 % Hg was found to be present compared to 28.5 % expected, confirming that essentially no complex was produced.

Attention was then transferred to 18-Crown-6, the reasoning being that the absence of the electron-withdrawing aromatic nuclei would, perhaps, enhance the electron-density at the oxygen atoms, thus giving rise to complexes that were more stable.

The procedure adopted to produce complexes of $CdCl_2$ and $HgCl_2$ with 18-Crown-6, along with the detailed results of the structural analyses, forms the main body of this thesis, and will be found in Section 2.

After the synthesis of the $CdCl_2$ and $HgCl_2$ complexes, attempts were made to synthesize a $ZnCl_2$ adduct of 18-Crown-6. A white solid was produced, following the same procedure as outlined in 2.1 for $CdCl_2$. At this point in time the nature of this product has not been pursued, nor have suitable crystals been obtained for diffractometry.

A complex of dicyclohexyl 18-Crown-6 with $HgCl_2$ has been prepared, using 1-butanol as solvent and the same technique used to prepare the 18-Crown-6·$HgCl_2$ complex. The appearance of this product is similar to that of the dibenzo-18-Crown-6 compound and recrystallization from another solvent, such as acetonitrile, or an alternative procedure for formation of the complex, will be required in order to obtain crystals for further study.

Finally, the adduct of $CdCl_2$ with 1-10-dithia-18-crown-6 has been prepared using the technique of 1-butanol solution of the ether floating on an aqueous solution of $CdCl_2$. The product is crystalline in nature, well-formed and showing regular extinctions between crossed polars. The structure of this complex will be the subject of another study.